PHOTOGRAPHIC

SCIENCE AND ENGINEERING

John Eggert — A Biographical Sketch 93

The Present Status of Photographic Development in Theory and Practice • *John Eggert* 94

The Influence of the Development Mechanism on the Color and Morphology of Developed Silver *T. H. James and W. Vanselow* 104

Some Properties of Developer Fog • *R. W. Swenson* 119

Internal Camera Vibrations and Their Effect on Resolution • *John W. Herold* 124

Technicalia Photographica • *Frank Smith* 132

Notes from the Editor 140

1958 Annual Conference Notice 140

JANUARY • 1958

Volume 1 • Number 3

Editorial Policy

Photographic Science and Engineering is dedicated to the advancement of the knowledge and application of photography and other directly related sciences. Its pages are open to all who wish to report on new studies dealing with the theory of photosensitive systems, the design of photographic instruments and apparatus useful in the treatment of photographic materials, photographic optics and illuminants, the use of photography for scientific or engineering measurement or recording, and photographic instrumentation and data recording. Only original papers should be submitted except on special invitation.

Manuscripts should be typed double-spaced on white bond paper with $1^1/_4$-inch margins all around. Literature references should be exact, and should include titles of papers and journals, names of authors, numbers of volumes and pages, and year of publication. Book references should include title of volume, names of authors, publisher, number of edition, year of publication, and chapter and pages cited.

Graphs, charts, and other line illustrations should conform to good usage such as given in the American Standards Association Document Y-15, "A Guide for Preparing Technical Illustrations for Publication and Projection." Continuous-tone photographs should be made on 8- by 10-inch glossy paper and should show pertinent image detail sufficiently clearly to permit reduction to fit a 3-inch column in this journal. All illustrations should be numbered in soft blue pencil on the back to correspond with captions typed on a separate page. Tables should also be submitted on separate pages appropriately identified. An abstract should accompany each manuscript.

All papers submitted for publication will be reviewed by members of the Editorial Review Board and if not accepted will be returned to the author, provided a self-addressed envelope and specific instructions are furnished. Published papers become the property of the Society and are protected by appropriate copyrights. Authors receive five copies of issues in which their contributions appear. Additional copies and reprints may be obtained. The Society does not assume responsibility for material in transit, nor guarantee publication of unsolicited material.

PHOTOGRAPHIC SCIENCE AND ENGINEERING

official publication of the
Society of Photographic Scientists and Engineers

JANUARY 1958
Volume 1, Number 3

EDITORIAL STAFF

Peter Krause, ***Editor***
Jennie H. Allen, ***Managing Editor***
Frank Smith, ***Feature Editor***
Robert H. Zappert, ***Feature Editor***
Willard W. Van Allen, ***Associate Editor***
Jean St. Thomas, ***Foreign Editor***

EDITORIAL REVIEW BOARD

T. H. James, ***Chairman***
R. S. Barrows
R. C. Davis
H. E. Edgerton
K. G. Leistner
J. A. Maurer
H. F. Nitka
J. H. Waddell

Photographic Science and Engineering is published six times a year, January, March, May, July, September, November, by the Society of Photographic Scientists and Engineers. Publication office at 20th and Northampton Streets, Easton, Pa. Address correspondence to the Society at Box 1609, Main Post Office, Washington, D.C. Subscription to non-members of the Society, $8.00 per year, members $4.00; single copies, $2.00 each. The Society is not responsible for the accuracy of statements made by authors and does not necessarily subscribe to their views. Application for entry as second class matter at the Post Office, Easton, Pa., is pending.

© Copyright 1958 by the Society of Photographic Scientists and Engineers, Inc. Permission to reprint any part of the contents, except in reviews and abstracts, must be obtained in writing from the Editorial Vice President.

Dr. John Eggert

Prof. Dr. phil., Dr.-Ing. E.h. John Eggert was the Guest of Honor of the Society of Photographic Scientists and Engineers at its Annual Conference, September 9–13, 1957, at Asbury Park, N.J. Dr. Eggert was made an Honorary Member of the Society and was presented with a silver plaque in recognition of his service to photographic science and engineering. At the Annual Banquet on September 12, after presentation of the award by President George T. Eaton, Dr. Eggert read an invited paper, "The Present Status of Photographic Development in Theory and Practice." This paper is published in succeeding pages of this journal.

Dr. Eggert was born in Berlin, Germany, on April 1, 1891. He was reared in that city and attended the University of Berlin and the Technische Hochschule, and was an assistant to the famous Nernst. He began lecturing on physical chemistry, photographic chemistry, colloid chemistry, and allied subjects in 1921 and was appointed a Professor at the University of Berlin in 1924. In 1921, he became also a Research Associate of the Agfa Company in Berlin and in 1928 was appointed Director of the Agfa Research Laboratories in Wolfen. After World War II, he taught briefly at the Technische Hochschule of Munich, but in 1946 he accepted appointment as head of the Photographic Institute of the Federal Institute of Technology in Zürich, Switzerland, a position that he occupies at present.

Dr. Eggert has gained world-wide recognition for his contributions in the fields of photographic research and teaching. He has been honored by many societies in many countries, and has been awarded, among others, the Gold Medal of the Photographic Society of Vienna and the Progress Medal of the Royal Photographic Society of Great Britain.

Dr. Eggert is author or co-author of several books and of numerous papers that pertain to all fields of photographic theory and practice. As Director of the Agfa Research Laboratories, he also supervised publication of the well-known annual, *Veröffentlichungen des wissenschaflichen Laboratoriums der Agfa*. In recent years, he has been very active in the organizing of the various International Congresses of Photography and has traveled and lectured widely on the Continent and in the United States.—*P.K.*

The Present Status of Photographic Development in Theory and Practice

JOHN EGGERT, *Photographic Institute of the Federal Institute of Technology, Zürich, Switzerland*

Early Photographic Development Processes

Photographic, physical-type development was first carried out by Louis Jacques Mandé Daguerre and William Henry Fox Talbot. Daguerre found in 1837 that vaporized mercury is preferably condensed on those parts of a silver iodide mirror which had undergone photolysis by a preceding strong exposure. In the daguerreotype process, the deposition of silver-mercury amalgamate on a latent image led to the formation of a visible image, and in the original experiments by Talbot (1841), it was the deposition of metallic silver on the exposed parts of silver iodide paper, after treatment with a gallic acid-silver nitrate solution, which produced an image. It is not surprising, therefore, that the influence of "nuclei" on the initiation of development processes has been taken into account from the very beginning in the various proposed theories of development.[1]

Theories of Photographic Development

Physical Development

In their study of the relation between physical development and the properties of development nuclei, Arens and Eggert found a relatively simple relationship[2] (Fig. 1) when nuclei are dispersed in gelatin layers and grown in a solution of silver nitrate and *p*-phenylenediamine in the presence of sodium sulfite. The following substances can serve as nuclei: Colloidally dispersed silver particles, produced by chemical reduction, having masses of 8×10^{-18} to 2×10^{-15} g, particles of gold or silver sulfide, and latent image silver. This photolytic silver may be formed by exposure of silver chloride, of ripened and unripened silver bromo-iodide, or of pure silver bromide formed in the presence of sodium nitrite, and can be transferred into the gelatin layer after removal of the halides. All these nuclei, although differing in chemical structure, origin, internal structure and mass, cause the deposition of equal amounts of silver in equal times. This is true only, however, if the number of nuclei is maintained constant per volume of emulsion, and if the growth of nuclei is carefully controlled. The "point" curve of Fig. 1 has a 45-degree slope over a rather wide range, i.e., the amount of silver deposited (as also the density of the layer) is proportional to the number of nuclei N; but when the number of nuclei become very large, this simple proportionality no longer exists, i.e., the deposition of silver decreases.

Chemical Development

Even without knowledge of this relationship, the analogy of photographic development and the initiation of crystallization from super-saturated solutions and melts by nuclei was noted by N. Ostwald (1893) and later by R. Abegg and K. Schaum (1899) and prompted them to explain chemical development in a similar way. Although this simple explanation of chemical development is valid for certain conditions, it soon had to be abandoned as a general theory. Strikingly, the silver deposit which is formed in the two types of development shows an entirely different structure: Physical development (Fig. 2a) normally yields compact plates of silver, whereas chemical development (Fig. 2b) yields mostly filament-like structures which very often form coils. Volmer[3] was the first to comprehend that chemical development is primarily a reduction (catalyzed by the latent image) of the solid silver halide by soluble developer substances, whereas the deposition of silver atoms formed in this process occurs as a second step.

Equilibrium and Reaction Rate

As in all chemical processes, two basic questions can be raised about this reduction: (1) Towards what side is the equilibrium shifted? and (2) what is the reaction rate? Of the developers normally used, except ferrous oxalate and related substances, all those based on organic chemical reducing agents irreversibly reduce the silver halide to metallic silver. Oxidized, i.e., exhausted developers cannot convert developed silver back to silver halide; in other words, they cannot act as photographic bleaching agents, or reducers. After sufficiently long developing periods both exposed and unexposed portions of the layer are reduced, whence the equilibrium between the Ag^+ ion and the reducing agent has been completely shifted to the side of the silver atom and oxidized developing substance. Since development should produce the greatest possible differentiation between exposed and unexposed portions of the sensitive layer the process

Presented as the invited lecture at the Annual Banquet of the Society, Asbury Park, N.J., 12 September 1957. Received 18 December 1957.

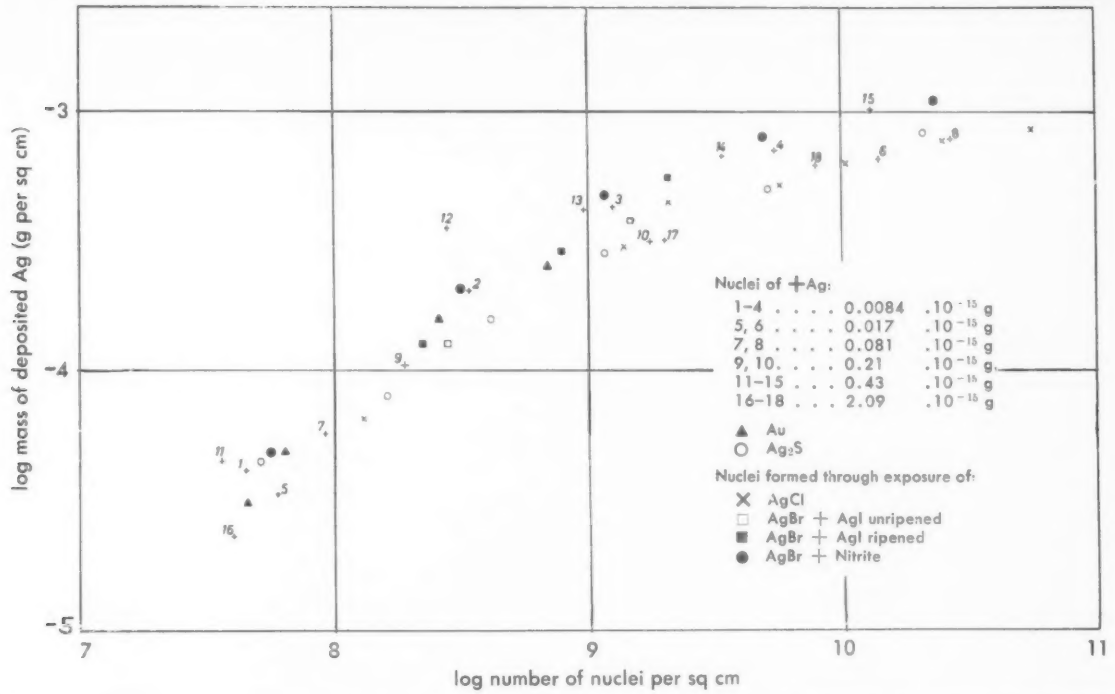
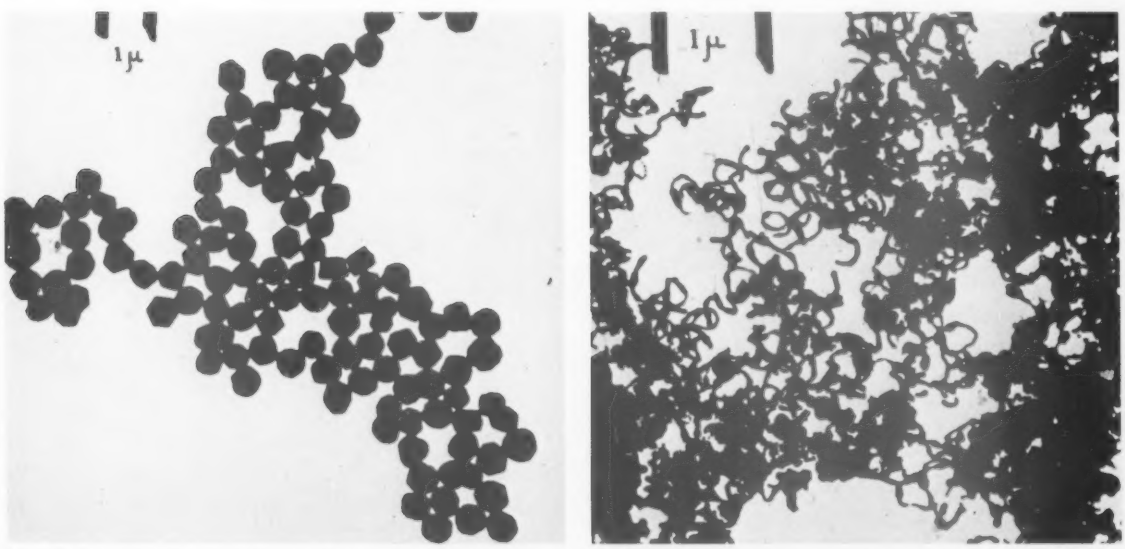


Fig. 1. The logarithm of the amount of silver (g per sq cm) deposited in 2 hours in a solution containing silver nuclei as a function of the logarithm of the number of nuclei per square centimeter



(a) Physical development of nuclei (after fixation), magnification ×10,000.

(b) Chemical development with metol-ascorbic acid developer for 24 minutes, magnification ×22,000.

Fig. 2. Electron micrographs of developed latent images. (Original prints of these electron micrographs were kindly supplied by Dr. T. H. James Eastman Kodak Company, Rochester, N.Y.)

must be stopped as soon as this maximum is reached and should never be carried to the point where equilibrium is established. This optimal time depends on the experimental conditions—especially concentrations, temperature, and agitation. The development process in practical photography, therefore, is not a problem of chemical equilibrium, but of chemical kinetics.

Constitution of a Chemical Developer

What characterizes a photographic developer? Obviously developers are not just reducing agents, because not all reducing agents are photographic developers. An alkaline stannous salt solution, for instance, does not differentiate between exposed and unexposed areas of the film, whereas an alkaline resorcinol solution discriminates but reduces the exposed silver halide so sluggishly that it cannot be considered a developer. A satisfactory definition may be approached either through specification of chemical structure or of the redox potentials of the developer substances.

In the latter part of the last century, a search was started for developing substances other than pyrogallol and ferrous salts and the number of suitable developing substances increased rapidly. As a result of the classical investigations by Andresen[4] and by the Lumière brothers with their associate Seyewetz, the following chemical configuration for developers was established in 1891:

Di-substituted products of benzene or naphthalene having $-OH$ and/or NH_2- groups in the ortho or para positions of the ring are developers. The NH_2- (but not the $-OH$) group can be substituted by radicals, such as $-CH_3$ or $-CH_2COOH$.

This simple and clear rule was extended by Kendall[5] to include α-hydroxyketones and substances of the structure $R-(C{=}C)_n-R'$, where n is an even integer and R and R′ are OH, NH_2, or NHR″ groups, R″ being any other radical. Although these rules apply widely, they do not cover all known developing substances. For instance, they do not include Kendall's[6] 1-phenyl-3-pyrazolidone (phenidone). Moreover, since the properties of some inorganic developers, and especially the developing properties of metal ions of higher valences, are not covered, it must be assumed that another, more general, rule exists.

Redox Potential

The principle can best be understood by considering the developing process electro-chemically, i.e., the redox potentials of developer systems in reference to the silver halides. The reduction of silver halides may be postulated to occur in two separate phases:

(a) $Red^- \rightarrow Ox + e^-$

(b) $e^- + Ag^+ \rightarrow Ag_o$

Red^- = reducing agent and Ox = oxidation product. These two reactions can be considered as current-producing processes akin to an electric cell that produces an electromotive force (emf), owing to a difference in potential, ΔE, between the silver electrode and the redox electrode (an inert conductor surrounded by a developer solution). Assuming that all processes are reversible, then according to the theory of W. Nernst (1889), the following equations are applicable to the silver electrode as measured against a standard hydrogen electrode:

$$E_{Ag} = E_{oAg} - \frac{RT}{F} \cdot \log \frac{C_{Ag^+}}{C_{Ag}}$$

and for the redox electrode:

$$E_{Red} = E_{oRed} - \frac{R.T}{n.F} \cdot \log \frac{C_{Ox}}{C_{Red}}$$

hence, the difference of potential ΔE of the cell is:

$$\Delta E = E_{Red} - E_{Ag}$$

R is the gas constant in electrical units (R = 8.314 W), T is the absolute temperature, F is the Faraday constant (F = 96490 Coulombs), n is the number of electrons involved in the process and C_{Red}, C_{Ox}, C_{Ag^+}, and C_{Ag} are the concentrations (or activities) of the reducing agents, oxidation products, silver ions, and silver atoms, respectively. If the concentrations of C_{Ox} and C_{Red} or C_{Ag^+} and C_{Ag} are equal, then $E_{Red} = E_{o.Red}$ or $E_{Ag} = E_{o.Ag}$, and the E_o values of both electrodes can be determined.

Bredig[7] was the first to use these calculations for the interpretation of the development process. He found that the redox electrode must have a more positive potential than the silver electrode in order to be photographically active. He also demonstrated the dependence of the ΔE value on pH, and that a reduction in pH reduces the effectiveness of the developer and produces smaller ΔE values.

Of the investigations which were carried out later, those by Reinders and Beukers[8] are noteworthy. These authors used mixtures of ferrous and ferric salts in the presence of complex formers such as citrate or malonate ions. From electro-chemical considerations one would expect development to start as soon as the potential ΔE of the cell differs from zero in the proper direction. That is, electrons would pass from the reducing ferrous ion to the silver ion of the silver bromide with consequent formation of ferric ion and metallic silver. Surprisingly, Reinders and Beukers found that development commences when the difference in potential ΔE amounts to 120 mv. Reinders explained this behavior as follows: The solution pressure of the extremely finely divided silver in the latent image (also the silver ion concentration C_{Ag^+} of the surrounding solution) must be larger than that of a compact silver electrode by a factor of about 30. There is no experimental proof, however, for this theory.*

Abribat,[9] who carried out similar experiments independently and at the same time as Reinders, concluded from the existence of such a critical potential difference ΔE for certain photographic layers that ΔE

* Only recently Trumpler and Hintermann observed that very thinly deposited silver layers have a lower electrochemical potential than compact silver electrodes (Thesis No. 2729, ETH, Zürich, 1957).

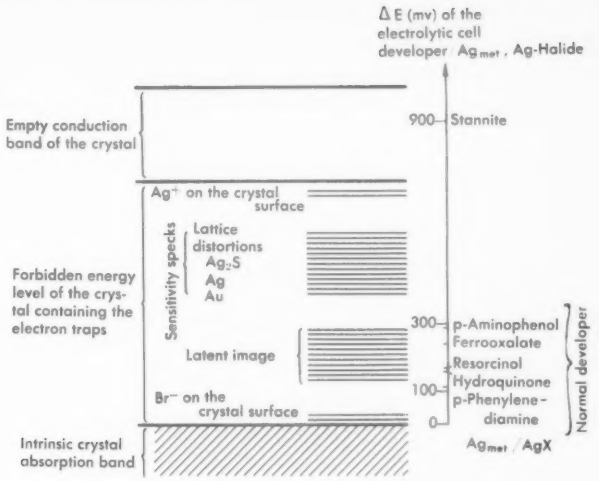


Fig. 3. Schematic arrangement of the energy levels of silver halide AgX adjacent to the scale of potential differences E(mv) of some reducing agents with reference to a metallic silver/silver halide electrode. (Overlapping of the separately drawn energy levels is possible.) Band model according to Mitchell[16]; ΔE values according to Jaenicke and Schott.[20]

cannot be explained theoretically but must be considered as empirically established, because the empirical value of ΔE is a characteristic property of a developer for a given layer. Any reducing system, even a weakly alkaline red Burgundy wine, must have developing properties when the value of ΔE is equal to or larger than the critical value for the layer in question. This is true regardless of the constitution of the active compound. Hence, the rule of Andresen-Lumière-Kendall covers only a special case within this general empirical observation.

In another investigation of three commercial photographic films, Abribat[9] found in 1949 that the value of ΔE is applicable to the development of the latent image as well as to the formation of fog. Therefore, the nuclei responsible for development of the latent image and those for the development of fog must be electrochemically, but not kinetically, equal.

Socher[10] reported the same facts in an earlier, less known publication in 1938. He worked with similar layers and colloidal suspensions of silver halide, but, in addition, made the important observation that binder-free suspensions behave normally and in accordance with theory, i.e., $\Delta E = 0$. In other words, the potential differences ΔE which Reinders and Abribat measured occur only in the presence of gelatin. Socher did not offer an explanation for the peculiar influence of the gelatin, but evidently a change in the electrochemical nature of exposed as well as unexposed silver halide in gelatins causes some shift in equilibrium.

The empirically determined, electrochemical criterion for a developer is not yet sufficiently well defined to permit a quantitative interpretation in terms of the band model. Qualitatively, however, each value of ΔE (Fig. 3) may be related to an energy level of the band model which can be occupied by sensitivity centers or development nuclei. The bromide ions of the crystal surface are in the lowest level; at a somewhat higher level are the latent image and sensitivity specks consisting of gold, silver, silver sulfide and crystal-defects; then follow the silver ions on the crystal surface; and finally, the conductivity band of the crystal* which occupies the highest level. Depending on the ΔE value of a developer, it is

* W. F. Berg was the first to propose the use of the band model for explaining the mechanism of the latent image formation.[11]

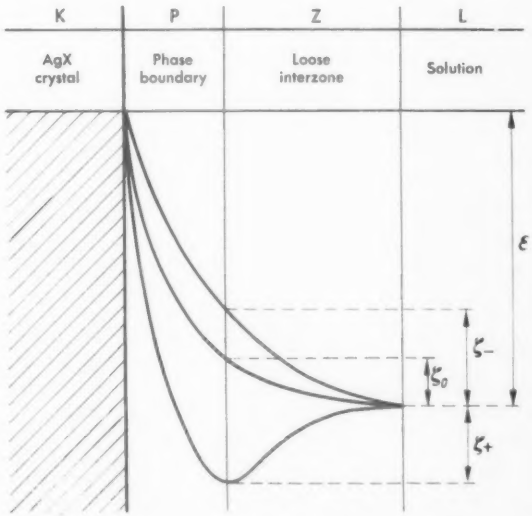


Fig. 4. Schematic arrangement of the potential difference ζ between the surface of a silver halide crystal and the bulk solution L. The phase boundary P and the loose interface zone Z are located between solution and crystal. The electrokinetic potential ζ, i.e., the potential barrier, is built up with changing signs. The standard potential ζ_0 increases, if the surface adsorbs anions, e.g., X^-, (ζ_-), and decreases for adsorption of cations, e.g., Ag^+, (ζ_+).

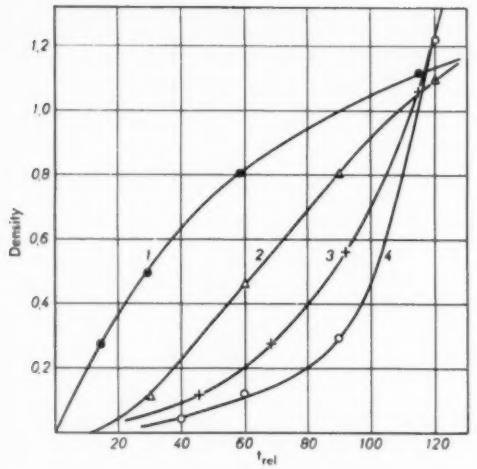


Fig. 5. Relative increase of optical density D with time of a specially exposed layer using developers with various charges of their reducing ions (according to James). (1) Charge 0, e.g., p-phenylenediamine; (2) Charge —1, e.g., p-aminophenol; (3) Charge —2, e.g., hydroquinone, pH = 12; (4) Charge —3, e.g., hydroquinone-monosulfonic acid.

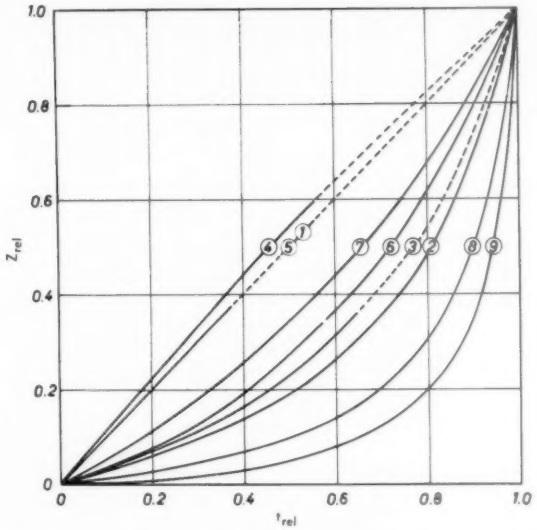


Fig. 6. Relative increase of I′-ion concentration ($=Z_{rel}$) with time during the reduction of IO_3'-ions (pH = 3) by 9 different developers: (1) hydroquinone; (2) pyrocatechol; (3) p-aminophenol; (4) monomethyl-p-aminophenol; (5) hydroxylamine; (6) hydrazine; (7) p-phenylenediamine; (8) monoethyl-p-phenylenediamine; (9) diethyl-p-phenylenediamine.

possible for its donated electrons to reach one of the sites of the crystal that act as electron traps or acceptors. For example, with a stannous salt developer, which has the highest ΔE value, the electrons may be assumed to wander directly into the conductivity band and to become active just as do electrons produced by light exposure. Thus, the crystal, regardless of the other levels and regardless of the existence of the latent image, is reduced to silver.[9] Quantitative relationships, however, have not been established; moreover, the failure of resorcinol to act as a developer under normal conditions cannot be explained as yet.

Developing Rate

Regardless of the lack of theoretical proof, this critical value of ΔE can be, at best, a necessary but not a sufficient condition; it refers only to the energy, not to the kinetic part of the developing problem. Again, in questions of chemical reactions, reversibility must be considered. In order to understand the approach to the kinetic problem, it is necessary to study more closely the structure of the phase boundary of the silver halide. Figure 4 shows the following conditions: Tightly held on the crystal surface K is a phase boundary, layer P. Between this boundary and the surrounding solution L is presumably a loosely bound interface Z, responsible for the electrokinetic zeta-potential. Its value depends on the electrical condition of the crystal surface. Whereas an ideal crystal of silver halide has no charge and may give the normal zeta-potential (ζ_o), the halide which is prepared for practical purposes is protected by the adsorbed gelatin molecules and, as a rule, is charged with halide ions that yield the more negative zeta-potential (ζ_-). Silver ions are adsorbed on the anions of the crystal lattice only in exceptional circumstances and then a positive zeta-potential (ζ_+) exists. The investigations of T. H. James[12] and his collaborators that followed earlier experiments by Schwartz and Urbach[13] have shown that the mostly negative potential barrier of the silver halide particles—the result of the negative zeta-potential—has a great influence on the kinetics of development. The greater the negative charge of the developer molecules the smaller their chance to penetrate the potential barrier and the longer the induction period.

As shown in Fig. 5, development starts immediately and without induction period when the developer molecule carries no charge, as with phenylenediamine (Curve 1), and is retarded more and more as the negative charge of the active ions increases (Curves 2, 3, 4). Similar results were obtained in an entirely different reaction—the oxidation of developers with iodate (Fig. 6). This is a type of Landolt reaction[14] which has been studied more thoroughly in Zürich. Since the iodate is reduced to iodine in an initial process (k_1) which is followed by a reduction to iodide ion in a second process (k_2), the reactions compete with each other kinetically. The ratio of the rate constants, $v = k_2/k_1$, which can increase from $v = 0.3$ for metol to $v = 160$ for diethyl-p-phenylenediamine, determines the shape of the resulting C_I ($=Z_{rel}$) vs. t_{rel}-curves, again for relative times, t_{rel}. In the first example, the iodate reduction is approximately

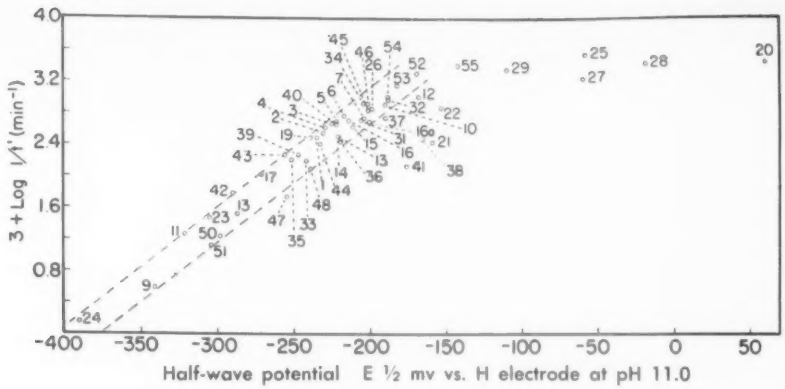


Fig. 7. Development rates vs half-wave potentials; t' = development time minus induction period.

three times faster, in the second 160 times slower than the iodine reduction.

Evidently development is accelerated when the negative charge of the zeta-potential barrier is lowered by the adsorbed cations. This can be done not only by silver ions but also by positively charged dye ions, by cations of quaternary ammonium salts or by tri- and tetra-amino or hydroxybenzenes.[15] After the developer molecule has passed this barrier and penetrated into the area of the boundary phase of the crystal, in other words after it has been adsorbed, the reduction of the silver halide crystal proceeds, catalyzed by developing centers. This mechanism is still under dispute. At any rate, the reducing agent first transfers its electron to the nucleus, somewhat in the manner illustrated in Fig. 3. Berg[11] assumes that in the crystal the silver ions near the sensitivity specks move to the speck where they are discharged and that the liberated halide ions migrate into the solution. The filamentary structure of the silver deposit becomes plausible because the silver ions are deposited always at the base of the speck.

This proposed model of chemical development also suggests a modification in the theory of physical development. Volmer[3] postulated that the nucleus can play the part of a catalyst in the reduction of soluble silver ions dissolved by the developer, and does not have to initiate the necessary crystallization of the super-saturated solution as was formerly thought. In harmony with the newer concept, it may be assumed that an electron is taken from the nucleus and that a silver ion of the solution is neutralized on this negatively charged particle. The electron by itself cannot reach the silver ion, however, and requires a conductive nucleus to overcome the high electric potential. Mitchell[16] in 1956 interpreted the formation of the latent image in this manner, expanding an earlier hypothesis of Eggert.[18] This model makes it clear that in physical development neither the mass nor the kind or the structure of the nuclei is of importance, but only their number. The difference in the shapes of the silver deposit—filaments in one instance and plates in the other—is not surprising under such different topographic conditions. This was explained very logically by Küster.[23]

The interpretation of chemical development requires some additional considerations. Hydroquinone, and probably other substances also, can only reduce a silver halide grain after traces of its oxidation product, quinone, have been formed. Staude and Brauer[19] proved by very painstaking experiments that hydroquinone is not adsorbed by unexposed or by exposed silver bromide. Quinone, however, is adsorbed only by exposed silver bromide—that is only by the latent image—and not by colloidal silver. Therefore, the necessary hydroquinone can be supplied to the grain only through quinone as an intermediate.

In order to separate the different influences of zeta-potential, adsorption and rate of all reactions, a special experimental technique was evolved by Jaenicke.[20] By separating the two functions of the nucleus, viz., electron acceptance from the developer and electron donation to the silver halide, an electric cell can be designed. By measuring the cell potential and current, information on the effects of ten partial steps in the development process can be collected. For instance, Jaenicke found for resorcinol the normal developer potential, but a very low rate of electron-transfer from the developer-ion to the nucleus; this is why resorcinol does not act as a developer.

More information on the kinetics of development was obtained in model experiments by Meidinger[21] and by Rabinowitsch[22] and their collaborators. One of the objects of these experiments was the evaluation of the average "lifetime" of exposed grains, i.e., how long does it take for development to start and when is development of a grain completed. To this end, silver halide grains were grown to a special size by very long physical ripening at high temperature and observed under the microscope. One of the many findings was that grains exposed in the solarization range have a longer "lifetime" than normally exposed grains, but that both types require the same time for complete reduction.

Mention must be made also of the numerous electronmicroscopic investigations of partially and completely developed crystals, such as those carried out at the Agfa laboratories.[23,24] Another type of model experiment was carried out by Fortmiller and James,[25] who employed liquid dispersions of silver bromide in

gelatin solutions instead of conventional, coated emulsions. This was done to avoid diffusion effects that occur when developing solutions penetrate a normal emulsion layer. Of the several problems studied in this fashion, the temperature dependence of the reduction of silver bromide by various developing substances (*p*-phenylenediamine, hydroquinone, and metol) merits particular attention. Fortmiller and James were able to determine the reaction rate constants (first order) and to calculate from their temperature dependence the activation energy values. The published figures show that the activation energy for the reduction of unexposed grains is twice, or at any rate larger than, that required for the reduction of exposed grains for which the latent image serves as a catalyst. This energy value is 20 kcal/mol for the formation of fog and 10 kcal/mol for the development of exposed silver bromide and checks satisfactorily, but only qualitatively, with the results of Fig. 3. The higher the level of the electron acceptors in the forbidden band of silver halide, the larger is the activation energy of the reduction process and the smaller its respective rate. Correspondingly, the temperature dependence of the rate is larger.[26]

In addition to the two qualitatively determined relationships between the band model and the value of ΔE (Fig. 3), and between the band model and the activation energy, Weissberger, James and eleven collaborators[27] found for 55 different color developers (substituted *p*-amino-dialkylanilines) a third relation between the developing rate V and the half-wave potential $E_{1/2}$ (Fig. 7). This was determined polarographically and found to be very close to the value ΔE (Fig. 1). The logarithm of the velocity V is proportional to the value $E_{1/2}$ and the reaction rate increases exponentially with increasingly positive $E_{1/2}$. On the other hand, since log V is inversely proportional to the activation energy it is evident that for the uncharged molecules of these developers the activation energy is a measure of the ease of transfer of an electron from the reducing agent to the nucleus. It is quite remarkable that the dropping electrode of the polarograph behaves like exposed silver halide in regard to the electron transfer. In six examples of the investigated series in which the $E_{1/2}$ value was more positive than approximately -170 mv, log V did not increase as expected, but stayed constant. Here the (constant) diffusion rate of the solution in the layer was smaller than the developing rate of the grain and determined the velocity of the whole process.

In all these considerations, one important factor that influences the development rate V must not be neglected, namely, the nature of the development nucleus itself. According to the Cabannes-Hoffmann Effect, the value V can increase or decrease continuously from a certain initial value until a certain density is obtained for equal exposure levels $I \times t$ (Fig. 8). V increases continuously with high-intensity, short duration exposures (broken curves) and decreases with low-intensity, long duration exposures (solid curves).

Comparing the behavior of chemical and physical development,[28] one can conclude that, in both, the number of nuclei is important. If, during a short exposure, many subnuclei are formed which become developable through action of the developer, then V increases autocatalytically from a low value. During a long exposure, full-size nuclei are formed and development starts immediately with a relatively large V value which decreases with time, because few developable nuclei are formed by the developer from subnuclei. In general, therefore, the development rate depends on the size frequency distribution of the

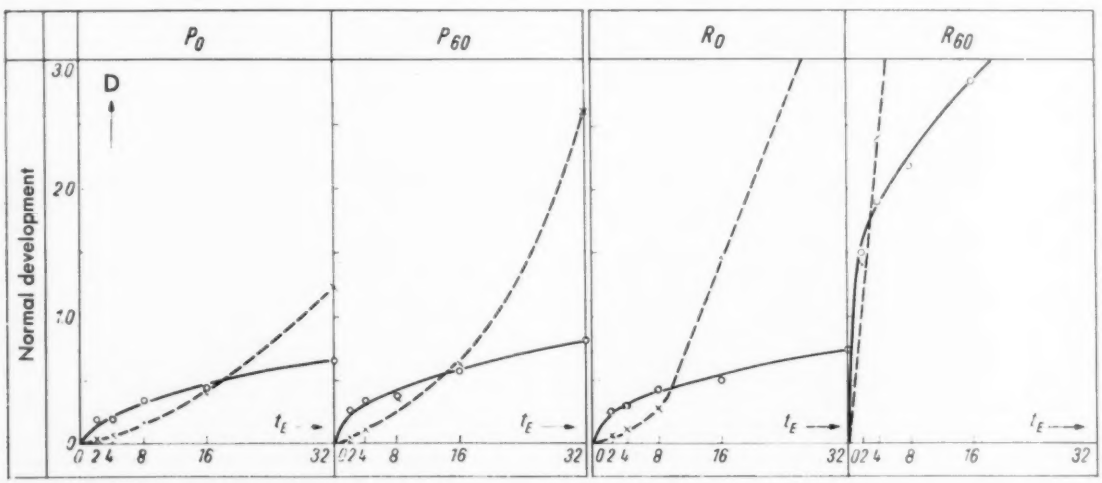


Fig. 8. Cabannes-Hoffmann Effect for normal development of four different photographic layers irradiated with equal energy (10 lux seconds). Solid curves indicate long exposure times (200 seconds); broken curves indicate short exposure times (6×10^{-4} seconds). Emulsions: (a) P_0 inert gelatin—0 minutes ripening; (b) P_{60} inert gelatin—60 minutes ripening; (c) R_0 active gelatin—0 minutes ripening; (d) R_{60} active gelatin—60 minutes ripening (according to J. Eggert and Y. Okamoto).

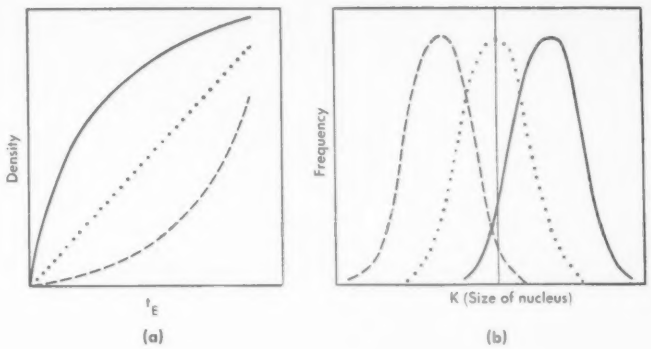


Fig. 9. (a) Frequency distribution schematic of curves D/t_E, derived from data in Fig. 8; (b) Frequency size distribution of nuclei per grain; K = critical size of nucleus (schematically indicated by center line). Exposure intensities are indicated as follows: broken curve — high intensity; dotted curve — medium intensity; solid curve — low intensity.

nuclei (Figs. 9a and 9b). If the size of the nucleus is equal to or larger than a critical size (K), the nucleus acts as a catalyst; if the size is smaller than K, the nucleus, now a subnucleus, does not act as a developer catalyst until it has increased to the critical size through action of the developer. This type of reduction has a lower rate (higher activation energy!) than normal development. High-intensity exposure yields more subnuclei, low-intensity more nuclei of the critical size.

The effective nuclei appear to have a surprising stability at times. For example, the latent image retains its catalytic properties even when the silver halide on which the latent image was formed is changed into another halide.[29] On the other hand, a change in size distribution of the nuclei probably is the cause of numerous photographic effects. In addition, the topographic distribution of the nuclei is bound to play an important part. Of the numerous publications that deal with these factors, those by Hautot, Debot, and Sauvenier[30] are noteworthy, as is also Arens's interpretation of the Sabattier effect as an internal latent image phenomenon.[31]

In conclusion, development, according to our present knowledge, may be defined as a heterogeneous catalytic reduction of silver ions by suitable substances. In the first step, the developer molecule penetrates the phase boundary area of the latent image nuclei in physical development or the silver halide grain in chemical development, passing the threshold of the zeta-potential, and in a second step is adsorbed. In a third step, in physical development, an electron is donated to a latent image nucleus by the developer; or, in chemical development, to the level of an existing acceptor according to the redox potential of the developer or according to the activation energy of the reduction process. On the now negatively charged site a neighboring Ag+ ion is reduced to a silver atom. More probably, according to Matejec (1956)[17] and also Mitchell,[16] a silver ion is first adsorbed on the sensitivity speck, imparting to it a positive charge. The developer electron then discharges the silver ion, augmenting the speck by one silver atom — the end result being the same as above. In chemical development, the full-size nuclei and, subsequently, the subnuclei initiate image formation, whereas the sensitivity specks induce fog.

Photographic Development in Practice

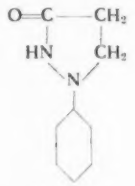
After a survey of the theory of development, its practical aspects should be considered, but since this field is even wider than the first, the discussion has to be restricted to the "classsical" development problems and must exclude such subjects as color development[32] and image transfer by diffusion,[33] even though the latter are in the limelight at present.

One-Substance Developers

Among the newer investigations of known one-substance developers, that by Roman[34] has aroused special interest. He continued some earlier work of Fuchs, Liesegang, and especially Rzmkowski, and explored simple redox systems such as bivalent metal ions and the conditions under which they exhibit developing properties. According to the ΔE values of the (Redox/Ag, AgBr)-cell, the following systems appeared to deserve attention: W^{6+}/W^{3+}; V^{3+}/V^{2+}; Ti^{3+}/Ti^{2+}; Cr^{3+}/Cr^{2+}. (Sn^{4+}/Sn^{2+} had to be excluded for well-known reasons.) Since chromium-ion systems give excessive fog, tungsten would require the use of hydrofluoric acid, and titanium is too unstable and too inactive, the only useful system is V+++/V++. Rasch and Crabtree[35] confirmed Roman's experiments and investigated the applicability of this interesting system. They found that a motion picture positive film which required 5 minutes development at 18 C in Kodak D-16 developer, developed in 20 to 40 seconds at 15 C in the very acid vanadium developer (0.4 m V++, 2.4/N-H_2SO_4, 0.6/N-KBr). Vanadium-developed sensitometric strips had somewhat steeper gradation and twice the speed of those developed in D-16 and a fog density of 0.1. The high developing speed is rooted in the positively charged V++ ions that easily overcome the zeta-potential barrier despite the high bromide ion concentration. A continuous regenerating procedure was worked out also, but the highly corrosive nature of the solution and its great oxygen sensitivity are formidable obstacles to its use in everyday practice.

New developer substances also have gained attention. The most important of these, discovered by Kendall, is 1-phenyl-3-pyrazolidone (phenidone).

James and Vanselow[36] have investigated the properties of developing solutions prepared with this developing agent which has the following structure



Phenidone

The activation energy of this substance for latent image reduction was determined to be 15 kcal/mol and that for spontaneous development (fog) 19 kcal/mol. It was also determined chromatographically that phenidone is adsorbed on silver bromide.

Composite Developers

In practice, composite developers are used to an overwhelmingly greater extent than one-component developers. The best-known composite developer is metol-hydroquinone. Abney recommended hydroquinone as a developer in 1880 and Bogisch and Andresen recommended metol in 1891. The much more important mixture of the two agents appeared anonymously in 1892, but the originator of the mixture cannot be determined with certainty, as was noted by Levenson[37] in his "memorial" paper on the "metol-sexagenarian." Originally, the thought of combining the advantages of both components, namely, the steep gradation obtainable with hydroquinone and the higher threshold-speed, but flatter gradation of metol, must have been decisive in the selection of the mixture. The properties of the two substances are not simply additive, however, and a surprising super-additivity results (Fig. 10). When the increase in density is plotted as a function of development time for the two individual components (Curves 1 and 2) and the sum of these two curves (Curve 3) compared with that of the combination (Curve 4), the combination is found to yield higher density for all developing times. This unexpected effect has been investigated repeatedly in other binary developing mixtures, especially by Levenson,[38] and various explanations of the phenomenon have been offered. On the basis of earlier findings by Tausch,[39] it might simply be assumed that metol is reduced first and that the hydroquinone reacts more slowly, owing to the double charge of its ions (Fig. 5). But hydroquinone will at once regenerate the oxidation product of metol, the *p*-methylquinone being oxidized simultaneously to quinone. Moreover, both oxidation products form the corresponding sulfonates in the presence of sodium sulfite. In principal, the super-additivity of the two-component system results from maintenance of the original metol concentration. When metol is used alone, its effectiveness gradually declines.

The action of the metol can also be performed by other substances—and even better. Axford and Kendall[40] found that metol can be replaced in the conventional metol-hydroquinone formula by 1-phenyl-3-pyrazolidone (phenidone) and at $^1/_7$ to $^1/_{10}$ the concentration. James has given the following explanation for the action of phenidone: (1) phenidone is easily regenerated by hydroquinone after it is oxidized by silver bromide; (2) the initiation of development lowers the potential barrier, which (3) is lowered again by the formation of quaternary ammonium ions. For these reasons, the amount of phenidone necessary to start and propagate the development process is very small and phenidone has begun to replace metol in the classical metol-hydroquinone mixture. Phenidone possesses the further advantage over metol of lower skin irritating activity.

Special Developers

Developers which are used for special purposes usually contain several reducing substances that perform different functions. For the determination of the distribution of the latent image on the surface and in the interior of the grain, James, Vanselow, and Quirk[41] recommend a sulfite-free developer composed of metol and ascorbic acid which is stable to oxidation and which acts only as the grain surface developer. The addition of sodium thiosulfate to this formulation converts it into an internal developer.

So-called fine-grain developers reduce the silver halide grain sparingly and only partially. Generally, this is accomplished by lowering the pH of the solution and by the addition of restrainers.

In order to secure maximum contrast, hydroquinone-*p*-formaldehyde (litho-type) developers are being used to an increasing extent in the graphic arts field. The first oxidation product of hydroquinone

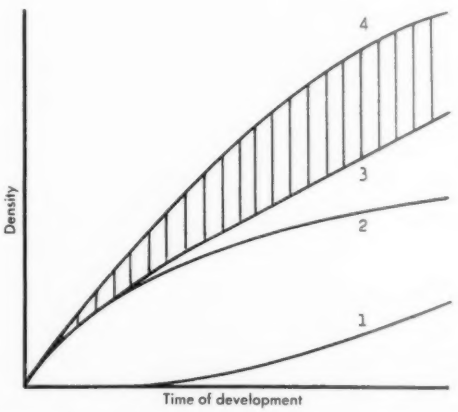


Fig. 10. The super-additivity of metol-hydroquinone is schematically indicated by the shaded area between Curve 3 and Curve 4. Curve 1 represents development with hydroquinone; Curve 2 represents development with metol or phenidone; Curve 3 represents the sum of Curves 1 and 2; Curve 4 represents the results actually obtained with the two-component mixture.

is a semiquinone. This, according to Yule,[42] is a very strong but unstable development accelerator which reacts easily with sulfite, whence it loses its valuable accelerator capability. Through the addition of formaldehyde, which is capable of combining with sulfite, the sulfite concentration can be kept low and the semiquinone made to remain active longer and to develop grains which contain subnuclei (infectious development).

Rapid development, yet another growing field, is preferably carried out with special equipment and at elevated temperatures (40 C) when special accelerators are not used.[15] Rapid development may also be followed by stabilization, i.e., the undeveloped silver halide may be converted into light stable compounds instead of being removed by fixation. Thiosulfate, thiourea, thiosemicarbazide, and alkaline iodide are used as stabilizers. Detailed procedures are found in the publications by Burkin[43] and Russell.[44]

This paper is intended to be a review only of photographic development. For detailed information the reader should consult the original literature cited as well as appropriate sections of recent reference works.[45]

Bibliography

1. Compare e.g. Luther, six papers (1898) discussed in *Z. wiss. Phot.*, Vol. 50, p. 4 (1955).
2. Arens, H., and Eggert, J., *Z. Elektrochem.*, Vol. 35, p. 728 (1929); Eggert, J., *Helv. chim. Acta*, Vol. 30, p. 2114 (1947); Arens, H., *Agfa Veröffentl.*, Vol. III, p. 32 (1933).
3. Volmer, M., *Z. wiss. Phot.*, Vol. 20, p. 189 (1921).
4. Eder, Lüppo-Cramer, *Handbuch d.r Photographie III*, Vol. 2, pp. 1–76, 6th ed., W. Knapp, Halle a.d.S., Germany (1930).
5. Kendall, J. D., *Proc. IX Congr. Internat. Phot.*, p. 227. Paris (1935).
6. ———, Brit. Pat. No. 542,502 (1940).
7. Bredig, G., *Eder's Jahrbuch der Photographie*, p. 19. Knapp, Halle a.d.S., Germany (1895).
8. Reinders, W., *J. Phys. Chem.*, Vol. 38, pp. 783, 796 (1934); Beukers, M. C. F., Dissertation, Delft (1934).
9. Abribat, M., *Sci. et ind. phot.* (2), Vol. 5, p. 140 (1935); ———, *Phot. J.*, Vol. 92B, p. 25 (1952); ———, Pouradier, J., and David, J., *Sci. et ind. phot.* (2), Vol. 20, p. 121 (1949).
10. Socher, H., *Z. wiss. Phot.*, Vol. 37, p. 51 (1938).
11. Berg, W. F., *Trans. Faraday Soc.*, Vol. 39, p. 115 (1943).
12. James, T. H., *J. Franklin Inst.*, Vol. 240, pp. 15, 83, 229, 327 (1945); *see also*, ——— and Kornfeld, G., *Chem. Rev.*, Vol. 30, p. 1 (1942).
13. Schwarz, G., and Urbach, F., *Z. wiss. Phot.*, Vol. 31, p. 77 (1932).
14. Eggert, J., *Helv. chim. Acta*, Vol. 36, p. 868 (1953); *also* Rohr, T., Thesis No. 2182, ETH, Zürich (1953).
15. James, T. H., and Vanselow, W., *Phot. Eng.*, Vol. 6, p. 183 (1955); for more examples of development accelerators, *see* Levenson, G. I. P., *J. Phot. Sci.*, Vol. 2, p. 77 (1954).
16. Mitchell, J. W., *Z. Elektrochem.*, Vol. 60, p. 557 (1956); ——— and Mott, N. F., *Phil. Mag.*, Vol. 2, p. 1149 (1957); ———, *Reports on Progress in Physics*, Vol. 20, p. 433 (1957).
17. Matejec, R., *Naturwiss.*, Vol. 43, p. 533 (1956).
18. Eggert, J., *Z. Elektrochem.*, Vol. 32, p. 497 (1926).
19. Staude, H., and Brauer, E., *Z. Elektrochem.*, Vol. 58, p. 129 (1954).
20. Jaenicke, W., and Schott, C., *Z. Elektrochem.*, Vol. 59, p. 956 (1955).
21. Meidinger, W., *Physik. Ztschr.*, Vol. 36, p. 312 (1935).
22. Rabinowitsch, A. J., Bogoyawlensky, A. N., and Zuew, Y. S., *Acta Physiochim. URSS*, Vol. 16, p. 307 (1942); *see also* Mees (*see* Ref. 45).
23. Küster, A., *Agfa-Veröffentl.*, Vol. 7, p. 268. S. Hirzel, Leipzig (1951).
24. Johann, I., and Klein, E., *Agfa-Mitteilungen*, Vol. 1, p. 24. Springer-Verlag, Berlin (1955).
25. Fortmiller, L. J., and James, T. H., *PSA Jour.*, Vol. 17B, p. 102 (1951); Vol. 18B, p. 76 (1952); Vol. 19B, p. 109 (1953).
26. James, T. H., Chap. 13 in Mees (*see* Ref. 45).
27. Bent, R. L., Dessloch, J. C., Duennebier, F. C., Fassett, D. W., Glass, D. B., James, T. H., Julian, D. B., Ruby, R. W., Snell, J. M., Sterner, J. H., Thirtle, J. R., Vittum, P. W., and Weissberger, A., *J. Am. Chem. Soc.*, Vol. 73, p. 3100 (1951).
28. Eggert, J., and Okamoto, Y., *Z. Elektrochem.*, Vol. 60, pp. 71 and 500 (1956).
29. According to not-yet-published experiments by Fischer, H., Thesis No. 2717, ETH, Zürich; and Eggert, J., and Fischer, H., *Z. Elektrochem.* (in press).
30. The numerous papers by the Liège scientists have been published in *Bul. Soc. Roy. des Sciences de Liège*, and in *Sci. et ind. phot.*
31. Arens, H., *Agfa-Veröffentl.*, Vol. 7, pp. 145, 151, 159. S. Hirzel, Leipzig (1954).
32. A good survey in: Weissberger, A., pp. 584–604, in Mees (*see* Ref. 45); Vittum, P. W., and Weissberger, A., *J. Phot. Sci.*, Vol. 2, p. 81 (1954); Contributions to *Color Development* I-XV from the Research Laboratories of Agfa Wolfen, published in Vol. in *Z. wiss. Phot.*, Vol. 50 (1955); finally, a remarkable study on color coupling by Eggert, J., and Frieser, H., *Z. Elektrochem.*, Vol. 60, p. 372 (1956).
33. Varden, Lloyd E., Chap. 16 in Neblette, C. B., *Photography, Its Materials and Processes*, 5th ed. Van Nostrand, New York (1952).
34. Roman, P., *Sci. et ind. phot.* (2), Vol. 23, p. 417 (1953).
35. Rasch, A. A., and Crabtree, J. I., *Phot. Sci. and Technique* (II), Vol. 1, p. 59 (1954).
36. James, T. H., and Vanselow, M., *Phot. Sci. and Technique* (II), Vol. 1, p. 77 (1954).
37. Levenson, G. I. P., *Funct. Photogr.*, Vol. 3, p. 8 (1952).
38. ———, *Proc. XI Internat. Congr. Pure and Applied Chemistry*, Vol. 1, p. 533, London (1947); ———, *Phot. J.*, Vol. 92B, p. 109 (1952); ———, *J. Phot. Sci.*, Vol. 1, p. 117 (1953).
39. Tausch, E., Thesis, TH, Berlin (1934); Lehmann, E., and Tausch, E., *Phot. Korr.*, Vol. 71, p. 17 (1935).
40. Axford, A. J., and Kendall, J. D., *J. Phot. Sci.*, Vol. 2, p. 1 (1954).
41. James, T. H., Vanselow, W., and Quirk, R. F., *PSA Jour.*, Vol. 19B, p. 170 (1953).
42. Yule, J. A. C., *J. Franklin Inst.*, Vol. 239, p. 221 (1945); Zünd, E., *Fachhefte f.d. Chemigraphie, etc.* (1952); Baines, H., *Process Engravers Monthly*, Vol. 61, p. 331 (1954).
43. Burkin, A. R., *Phot. J.*, Vol. 87B, p. 108 (1947).
44. Russell, H. D., *Phot. Eng.*, Vol. 2, p. 136 (1951).
45. Mees, C. E. K., *The Theory of the Photographic Process*, rev. ed. The Macmillan Co., New York (1954): see especially Chaps. 13–16, contributed by James and Weissberger.
Abribat, M., *Chimie physique des couches sensibles photographiques*. Presses universitaires de France (1954).
For the practical problems: Clerc, L. P., *La Technique photographique*, 5th ed., Paul Montel, Paris (1950); Mutter, E., *The technique of the negative and positive photographic processes*, Springer (1955).

PHOTOGRAPHIC SCIENCE AND ENGINEERING
Volume 1, Number 3, January 1958

The Influence of the Development Mechanism on the Color and Morphology of Developed Silver

T. H. James and W. Vanselow, *Research Laboratories, Eastman Kodak Company, Rochester, N.Y.*

Koerber concluded that the warmest tones in a developed image are obtained when the silver grains have a very loose structure. As the structure becomes more compact, the tone shifts towards blue-black. We have found that this conclusion is valid under some particular conditions, but not under others. Large changes in the color of the developed silver and in the morphology of the silver grains were obtained simply by varying the pH of the developer or by changing the developing agent. Two distinct types of silver deposit were obtained under two extremes of development conditions. The first type, obtained with a surface developer, is composed of filamentary silver. Its covering power for densities measured at 700 mμ is nearly independent of the degree of development of the grains beyond the early stages. The maximum density in the spectral range, 400–700 mμ, lies at 400 mμ. The color ratio, D(max)/D(700), decreases with increasing degree of development and approaches unity. The second type, obtained with a *p*-phenylenediamine developer, shows no evidence of filamentary structure. Its covering power for densities measured at 700 mμ decreases constantly with increasing degree of development of the grains. The maximum density in the spectral range, 400–700 mμ, lies at a wavelength longer than 400 mμ. The color ratio decreases to a minimum well above unity and subsequently remains substantially constant or increases.

The preceding characteristics can be recognized to varying degrees in the images produced by the different developers studied. The type of image produced, or the relative mixture of the two types, can be correlated with the relative extent to which solution-physical development occurs during the formation of the silver deposit.

The color of finely divided silver can vary widely, depending on the conditions under which it is formed. Numerous studies have been made of the color of colloidal silver. Some of the older work has been summarized by Mees.[1] Recently, Wiegel[2] has made an extensive study of the absorption spectra of colloidal silver preparations over a range of particle sizes and has obtained electron micrographs of the particles. The colors of his silver sols, in relation to particle size, are listed in Table I.

The silver grains which make up the developed image in most photographic materials are larger in size than the colloidal particles studied by Wiegel, although the diameters of individual silver filaments usually fall within Wiegel's range. The color of the developed image depends on the photographic material used, but it also can be varied considerably for one material by suitable changes in the conditions of development. Certain agents can be added to the developer which will change the tone of the developed image. The patent literature discloses several classes of blue-black addition agents and antiplumming agents.[3]

Two papers on the relation of color to the structure of the silver deposit were presented at the International Conference on Scientific Photography at Cologne in 1956. Koerber[4] studied electron micrographs of silver obtained from silver chlorobromide and silver bromide grains, developed under various conditions. He concluded that the size of the silver grain, rather than the morphology, was the important factor in

TABLE I
Color and Particle Size of Silver Hydrosols (after E. Wiegel)

Transmission Color	Scattered Light Color	Particle Size Region, mμ
Yellow	Blue	10– 20
Red	Dark Green	25– 35
Purple-red	Green	35– 45
Violet	Yellow-green	50– 60
Dark Blue	Mud Yellow	70– 80
Light Blue	Red Brown	90–100
Gray Green	——	120–130

Communication No. 1925 from the Kodak Research Laboratories, presented at the Annual Conference, Asbury Park, N.J., 12 September 1957. Received 19 October 1957.

determining the image tone when the silver halide grains were very small, i.e., 10–50 mμ. The structure of the developed grain was an important factor for the larger-grain emulsions. The warmest tones corresponded to a very loose structure of the developed silver. As the structure became more compact, the tone shifted towards blue-black.

Cassiers[5] studied the color of silver deposits formed by the inversion-transfer process. Blue-black tones were obtained by use of certain heterocyclic mercaptans in the developer under conditions which gave yellow-brown silver in the absence of the mercaptans. Electron micrographs showed no significant difference either in the average size or size-distribution of the silver particles in the blue-black and yellow-brown images. X-ray diffraction analysis showed that the blue-black image particles were formed of primary crystallites of smaller dimensions than the brown-image particles and the crystal network was more disordered. He suggests that the higher degree of disorder in the particles of the black image produces surface deformations which modify the optical properties of the surface. The surface, rather than the over-all particle size, largely determines the optical properties of the silver deposit.

This suggestion is in agreement with Jelley's explanation[1] for brownish tones in silver images. He suggests that the light which passes through the photographic image is reflected many times from minute facets on the silver grain, and, at each reflection, the light becomes yellower because of the surface color of the silver. Reduction of the reflecting power of the silver makes the image more nearly neutral.

In the present investigation, we have worked principally with a high-contrast, motion-picture positive emulsion and a series of developers which contained either 100 g sodium sulfite and 1 g potassium bromide per liter, or contained 10 g l-ascorbic acid in place of the sulfite. By simply changing the pH of the solution and the nature of the developing agent, it was possible to change markedly the visual appearance and the absorption spectrum of the developed silver. These changes have been correlated with the relative extent to which solution-physical development occurs (in the absence of added tone-modifiers).

Two extreme types of silver deposits were recognized in the present work. The first type is composed of filamentary silver. Its covering power (density/silver per unit area) for densities measured at 700 mμ is nearly independent of the degree of development of the grains beyond the early stages. (The covering power of a silver bromide negative-type material decreased with increasing density, however.) The maximum density lies at 400 mμ or shorter, and the ratio of the maximum density to that measured at 700 mμ decreases with increasing degree of development. This type o' silver deposit is produced by the surface developers where development proceeds primarily by the direct mechanism.

The second type shows no evidence of filamentary structure. Its covering power for densities measured at 700 mμ decreases constantly with increasing degree of development of the grains. The maximum density lies at a wavelength longer than 400 mμ, and the ratio of the maximum to the density measured at 700 mμ decreases to a minimum which is well above unity and subsequently remains constant or increases. This type of silver is produced when development proceeds primarily by the solution-physical mechanism. It is readily obtained with *p*-phenylenediamine–sulfite solutions of pH 6–10, but can be obtained with other developing agents as well, under proper conditions.

The characteristics of the two types of silver can be recognized to varying degrees in the images produced by the different developers studied. The color of the deposits appears to be determined primarily by the structure of the silver surface rather than by the over-all size of the developed grain. We have obtained silver deposits which differed markedly in the average size and size-distribution of the individual particles, but showed almost identical spectral characteristics.

Experimental Procedure

The principal photographic material used in the present investigation consisted of two coatings of the same preparation of high-contrast, motion-picture-positive, silver iodobromide grains. One was a normal coating at a spread of 384 mg silver per square foot (Coating *A*). The second was a coating of the same weight of silver halide but with the addition of 4.5 mg per square foot of a Carey-Lea-type silver sol (Coating *B*). For image development, Coating *A* was exposed for 15 minutes on each side to a 6-watt lamp, operated at 115 volts at a distance of 140 cm from the film. Substantially all the grains in the coating were made developable by this exposure, which was not enough to produce solarization. A few experiments were performed with a simple, "boiled," pure bromide, negative-type emulsion.

Development was carried out at 20.0 C with vigorous nitrogen-burst agitation. The developed strips were rinsed in 2 per cent acetic acid for 10 seconds, then fixed for 2 minutes successively in each of two fixing baths (Kodak Fixing Bath F-5). Alum was omitted from the first fixing bath in the experiments in which phosphate was used as buffer in the developer. Total (integral) density measurements were made on each sample over the spectral range 400–700 mμ, and silver analyses were made on all samples.

Coating *B*, which was used to determine solution-physical development rates, was developed without exposure. The procedure for measuring the rates of solution-physical development has been described previously.[6] In principle, it involves solution of the silver halide in the developer and subsequent physical development of the silver at the colloidal silver nuclei. In some experiments, postfixation physical development was used to develop an exposed, fixed-out emulsion, or a simple coating of colloidal silver in a gelatin layer.*

* The electron micrographs used in this investigation were prepared by C. F. Oster, Jr., of these Laboratories.

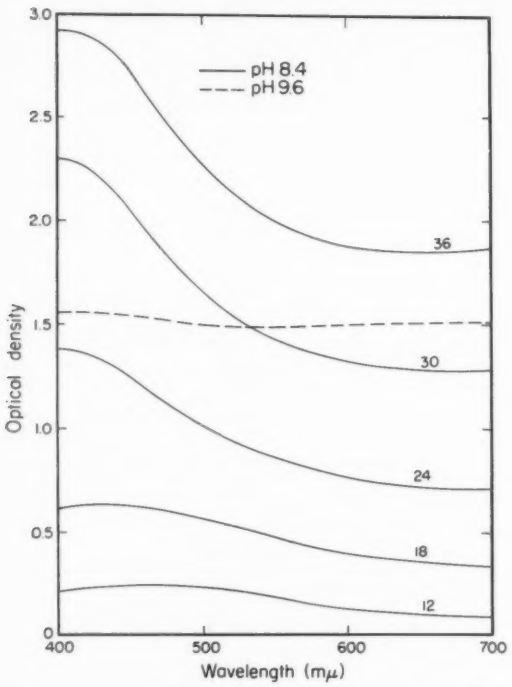


Fig. 1. Spectrophotometric curves for silver developed by the Elon–ascorbic acid–KBr solutions. ——— pH 8.4; development times specified on curves. – – – pH 9.6; development for 40 min at pH 9.6 and 20 C.

Experimental Results

p-*Methylaminophenol Developers*

Exposed strips of Coating *A* were developed for various times in a dilute, slow-acting surface image developer[7] of the following composition: Kodak Elon Developing Agent* (*p*-methylaminophenol sulfate), 0.28 g; l-ascorbic acid, 2.78 g; potassium bromide, 1.0 g; 0.1 *M* borax, 153 cc; total volume, 1 liter; pH 8.4.

The solid curves in Fig. 1 show the spectrophotometric curves (total densities) of the silver deposits obtained by development for the times indicated on the curves. In the early stages of development, the curve shows a maximum in the visible region (about 460 mμ). Electron micrographs (Fig. 2a) show that the silver at this stage is in the form of very small and apparently compact particles, 20–50 mμ in diameter. The maximum shifts to shorter wavelengths as the time of development increases, and lies at 400 mμ or less for development times of 24 minutes and longer. The transition is accompanied by a marked change in the appearance of the silver deposit under the electron microscope. The deposit for 18 minutes' development already is largely filamentary in character, although some tiny, roughly spherical or ellipsoidal particles are present. The deposit for 24 minutes or more (Figs. 2b, 2c) is almost entirely filamentary. The filaments become more tightly packed as the time or degree of development increases. Fully developed grains are evidently still composed of filamentary silver, but are more compact. Figure 2d shows silver formed by full development for 40 minutes in a more active surface developer consisting of 2.5 g Elon, 10 g l-ascorbic acid, and 1.0 potassium bromide per liter at pH 9.6. The broken curve in Fig. 1 represents the silver deposit of fully developed grains for an exposure such that only about one-third of the total number of grains developed. The deposit is spectrally almost neutral.

The ratio of the maximum density to the density measured at 700 mμ decreases with increasing time of development, as shown in Table II. The covering power for densities measured at 700 mμ increases with increasing density in the early stages of development, but becomes almost independent of density for densities above about 0.2.

Another set of experiments was carried out with solutions which contained 0.10 *M* Elon, 100 g sodium sulfite, and 1.0 g potassium bromide per liter. The pH was adjusted to the desired value with additions of sulfuric acid, sodium hydroxide, or sodium metaborate. The absorption spectra of the silver deposits showed no maximum in the visible region and were of

* "Elon" is a trademark registered in U.S. Patent Office.

TABLE II

Development of Exposed Coating *A* by the Elon–Ascorbic Acid–Potassium Bromide Developer at pH 8.4

Time (min)	D(max)	D(400)	D(700)	Silver mg/sq ft	D(max)/D(700)	D(700)/Silver
8	0.06	0.05	0.00	4.9	——	——
12	0.21	0.17	0.055	8.2	3.82	0.0067
18	0.60	0.57	0.29	20	2.07	0.0145
24	1.34	1.34	0.67	45	2.00	0.0149
30	2.24	2.24	1.25	86	1.79	0.0145
36	2.87	2.87	1.83	127	1.57	0.0144
130*	1.20	1.20	0.94	——	1.27	——
40**	1.52	1.52	1.48	——	1.03	——

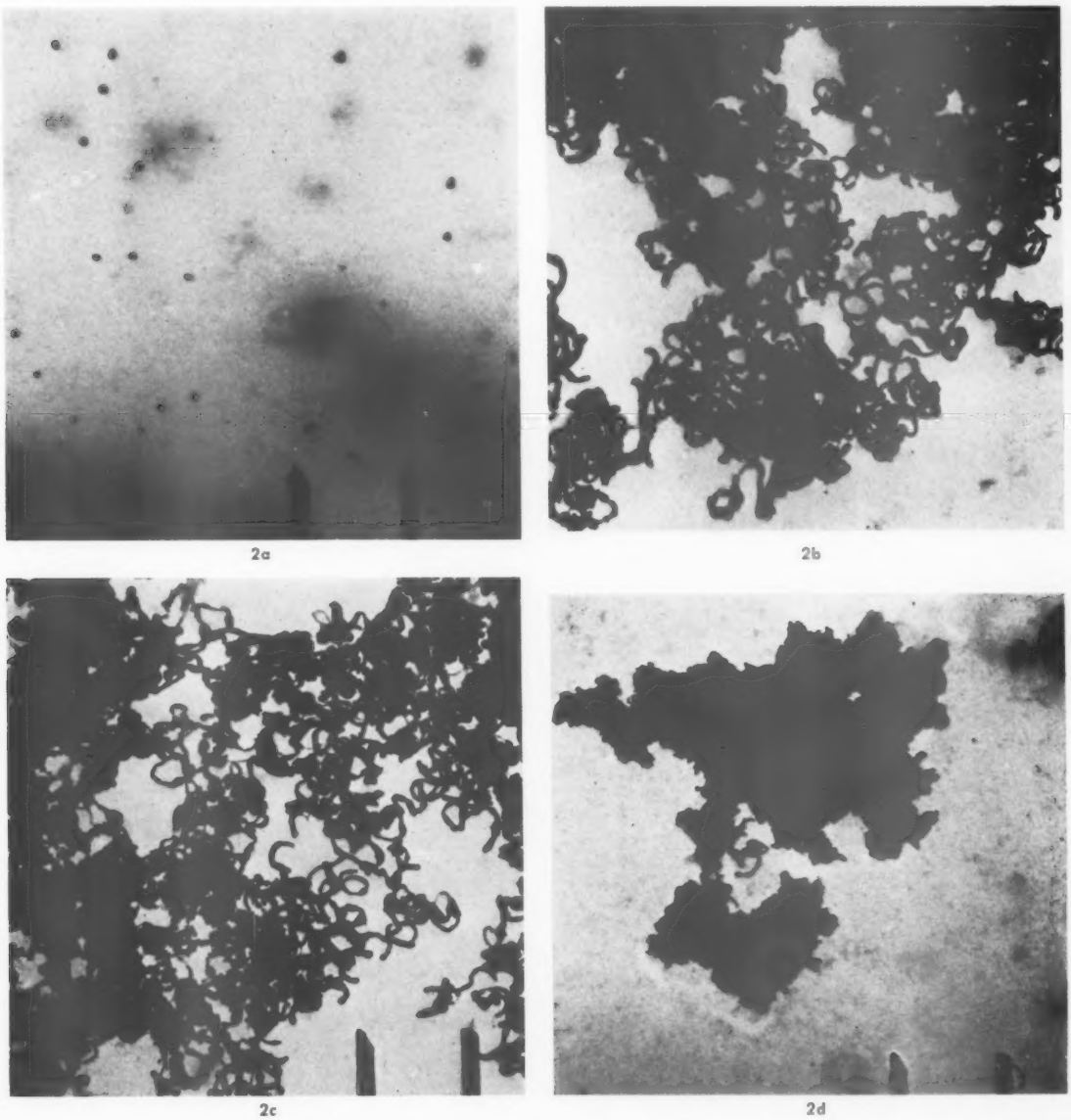
* Film exposed at log E = 1.15 on Eastman Sensitometer, Type IIb.

** Developed at pH 9.6, film exposed to produce development of approximately one-third of total grains.

the general form shown in Fig. 3. The developed silver was filamentary.

The ratio of the density measured at 400 mμ to that at 700 mμ can be taken as an indication of the "color" of the silver deposit when the spectrophotometric curve shows no maximum between these wavelengths. The drop in density over this region actually occurs largely or wholly between 400 and 600 mμ. Data for development by the Elon–sulfite–KBr solutions at various pH levels are given in Table III. For a given pH, the density ratio decreases as the time of development increases. For varying pH and development to a fixed amount of silver, the ratio decreases with increasing pH. The covering power for densities measured at 700 mμ reaches a maximum value for each pH level at a rather low density and is nearly independent of density for longer times of development. The covering power decreases with decreasing pH in the range 7.5–6.5.

The variation in image color with pH, for equal



2a 2b 2c 2d

Fig. 2. Electron micrographs of developed silver. 2a corresponds to 12-minute curve of Fig. 1; 2b to 24-minute curve; 2c to 36-minute curve; and 2d to broken curve. The parallel bars indicate a distance of one micron.

amounts of developed silver per unit area, can be correlated with the variation in the relative amount of solution-physical development. Table IV lists the rates of total image development, solution-physical development, and the ratio of the two for the Elon developers and several others. The rates are expressed as the reciprocal of the time required to develop the second 10 per cent of the total silver present ($t_{20\%} - t_{10\%}$). The ratio of the two rates increases with increasing pH. This means that the relative importance of solution-physical development decreases with increasing pH. The divergence of the image silver from spectral neutrality for development of a fixed amount of silver likewise decreases with increasing pH. Hence, the divergence from neutrality increases with increasing relative amount of solution-physical development.

The silver image obtained at pH 10.0 is nearly neutral, even during the early stages of development. The reason for this is that, unlike the situation at the

TABLE III

Development by 0.1 M Elon, 100 Grams Sodium Sulfite, and 1.0 Gram Potassium Bromide per Liter at 20.0 C

pH	Time (min)	D(400 mμ)	D(700 mμ)	Silver mg/sq ft	D(400)/D(700)	D(700)/Ag
6.5	6	0.06	0.01	4.5	—	—
	12	0.45	0.20	15.7	2.25	0.0127
	15	0.82	0.365	28.5	2.25	0.0128
	18	1.28	0.58	47.0	2.20	0.0123
	21	1.70	0.81	66	2.10	0.0123
	26	2.40	1.29	99	1.86	0.0130
6.9	3.25	0.36	0.15	14.0	2.40	0.0107
	4.5	0.95	0.47	33.4	2.02	0.0141
	6	1.61	0.93	64	1.73	0.0145
	8	2.40	1.57	104	1.53	0.0151
	10	2.71	2.04	149	1.33	0.0137
	12	2.85	2.38	169	1.20	0.0141
7.55*	1	0.31	0.14	11.7	2.21	0.0128
	2	1.04	0.62	38.7	1.68	0.0160
	2.5	1.83	1.27	80	1.44	0.0159
	3	2.56	2.03	134	1.26	0.0151
	4	2.85	2.57	178	1.11	0.0144
10.0	0.12	0.52	0.49	36.8	1.06	0.0133
	0.25	1.10	1.00	61	1.10	0.0163
	0.37	1.91	1.70	113	1.12	0.0150
	0.50	2.22	2.11	136	1.05	0.0155
	0.75	2.87	2.86	186	1.00	0.0154

* Some *p*-methylaminophenol precipitated when the pH was adjusted to this value.

TABLE IV

Rates of Image Development and Solution-Physical Development — Solution: Developing Agent, 100 Grams Sodium Sulfite, 1.0 Gram Potassium Bromide per Liter at 20.0 C

Developing Agent	pH	Rate of Image Dev.	Rate of Soln. Phys. Dev.	Ratio: Image/Soln.
0.1 *M* Elon	6.5	0.17	0.068	2.5
	6.9	0.5	0.17	3.0
	7.55	2.1	0.17	12.8
	10.0	8.3*	0.17	⩾50.0
0.1 *M* *p*-Phenylenediamine dihydrochloride	6.4	0.027	0.043	0.64
	7.0	0.105	0.20	0.53
	8.3	0.31	0.59	0.53
	10.2	0.59	0.93	0.63
	12.0	10.0*	7.7	⩾1.30
0.2 *M* Hydroquinone	8.2	0.014	0.08	0.18
	8.6	0.11	0.16	0.65
	9.6	2.2	0.16	13.8
0.2 *M* Catechol	8.5	0.063	0.069	0.91
	9.5	1.25	0.14	8.9
	10.0	4.2	0.16	26.1
0.2 *M* Hydroxylamine	10.65	0.16	0.37	0.44
	11.8	4.5	0.36	12.7

* Rates largely diffusion-controlled.

lower pH levels, the rate of development by this solution at pH 10.0 is largely controlled by the rate of diffusion through the gelatin layer. Even the low densities represent grains which have been developed nearly to completion.

p-Phenylenediamine Developers

Development by a solution of 0.1 *M* *p*-phenylenediamine dihydrochloride, 100 g sodium sulfite, and 1.0 g potassium bromide over the pH range, 6.3–10.2, produces a silver deposit which is quite different in appearance from that obtained with the Elon solutions. Figure 4 shows typical spectrophotometric curves (total densities) for silver produced by different times of development at pH 6.4, 8.3, and 12.0. The curves for the two lower pH levels show a pronounced maximum at about 460 mμ. The specular density curves over the same pH range are similar in form and the maximum is at about 500 mμ.

The form of the silver particles responsible for these curves is shown in Figs. 5a, 5b, and 5c. Figures 5a and 5b show the particles obtained by 47 and 195 minutes' development at pH 6.4. The size clearly increases with time of development, even though the shape of the spectrophotometric curve remains substantially the same. The average particle size in Fig. 5b is about 0.25 μ. Figure 5c shows an electron micrograph of silver particles developed at pH 7.0. These particles have been shadowed to indicate the third dimension. The ratio of the length of the shadow to the thickness of the particle is 3:1. The smaller particles are nearly spherical in form. The thickness of most of the particles, however, lies between one-half and two-thirds the diameter of the projection area.

The curves obtained at pH 10.2 are similar to those for the lower pH levels, although the position of the maximum is at somewhat shorter wavelengths. The silver deposit produced by development at pH 12.0, however, shows no maximum in the visible, and resembles that produced by the Elon developer at pH 10.0 The form of the developed silver is distinctly filamentary, as shown in Fig. 5d.

Numerical data for the densities and amounts of silver obtained by development for various times and at various pH levels are given in Table V. The ratio of the density at the maximum to the density at 700 mμ does not show the continuous drop with increasing time of development that had been observed with the Elon developers. The ratio actually passes through a minimum and then increases for the pH range, 6.3–8.3. The covering power measured for densities at 700 mμ decreases continuously with increasing amounts of developed silver, instead of remaining substantially constant, as in the case of Elon development. On the other hand, both the "color ratio" and the covering power for development by *p*-phenylenediamine at pH 12.0 follow the pattern observed for Elon development.

The silver developed by the low-pH *p*-phenylenediamine solutions closely resembles that obtained by postfixation physical development in respect to the spectral variation of density, and the variation in the

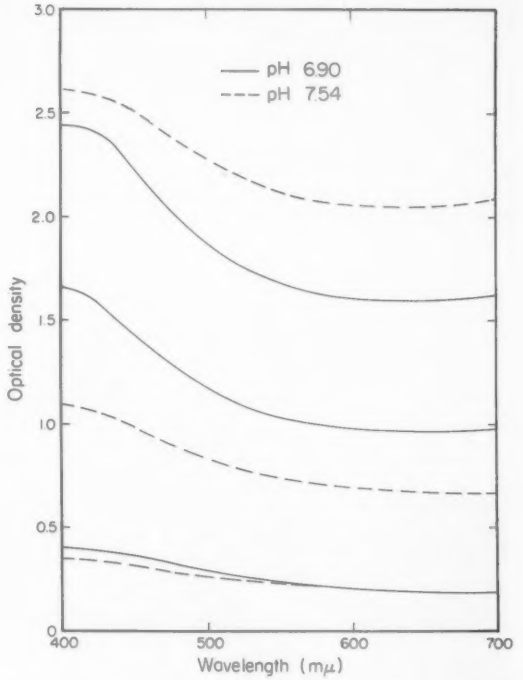


Fig. 3. Spectrophotometric curves for silver developed by the Elon–sulfite–KBr solutions. ——— pH 6.90, development times 3.25, 6, and 8 minutes at 20 C. – – – pH 7.54, development times 1, 2, and 3 minutes at 20 C.

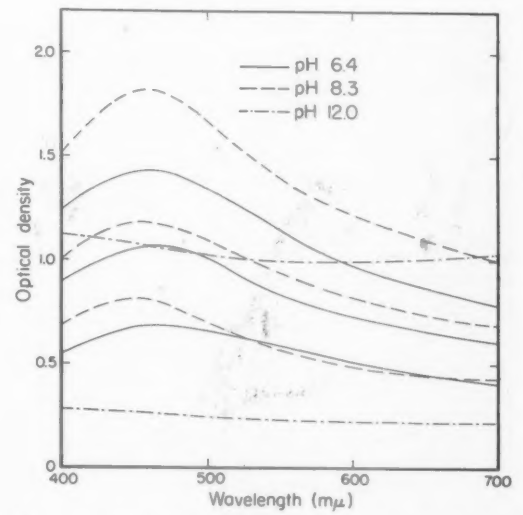
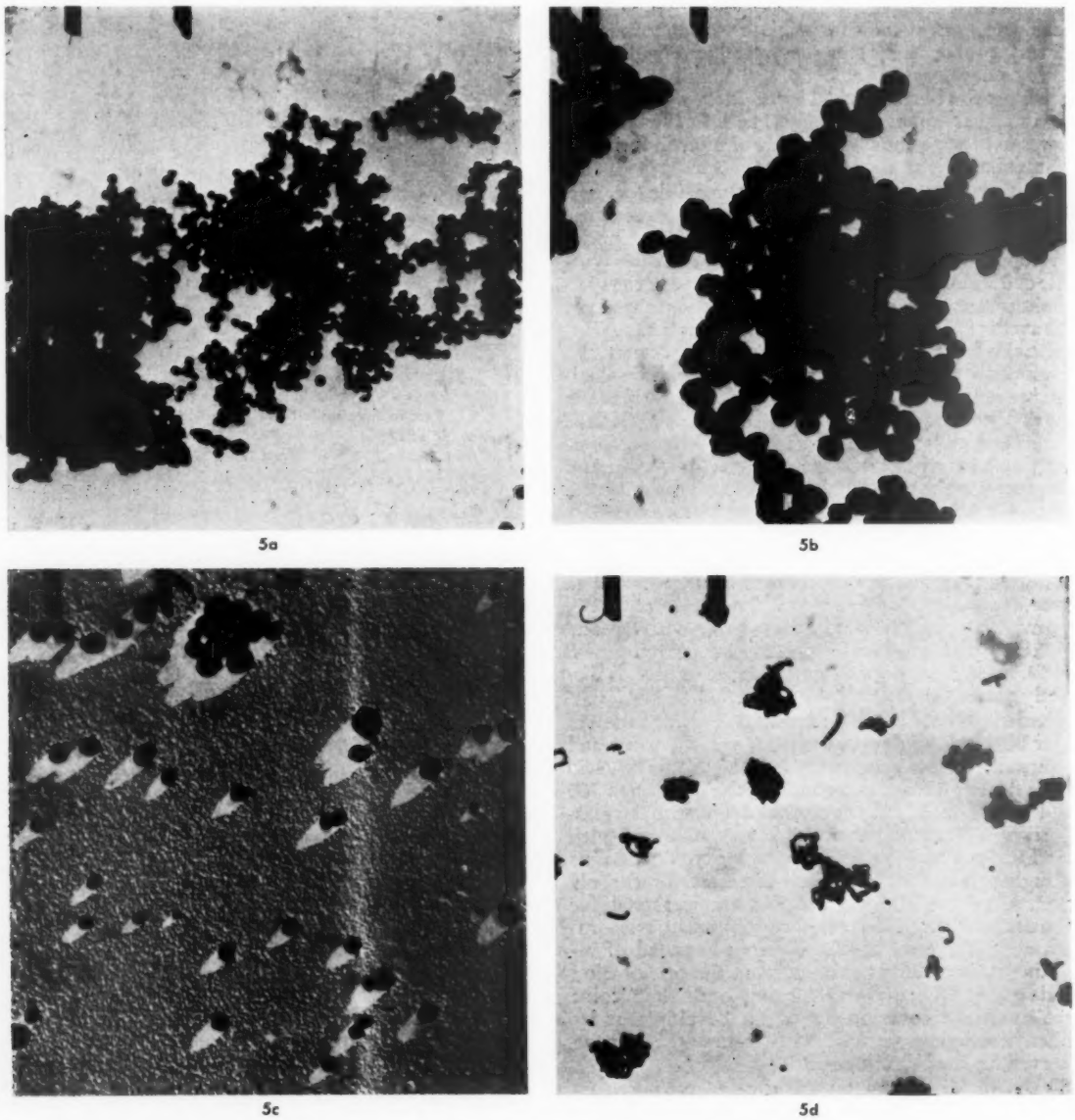


Fig. 4. Spectrophotometric curves for silver developed by the *p*-phenylenediamine–sulfite–KBr solutions. ——— pH 6.4, development times 47, 105, and 195 minutes at 20 C. – – – pH 8.3, times 5, 7.5, 14.5 minutes at 20 C. –·–·– pH 12.0, times 0.11, 0.25 minutes.

"color ratio" and covering power with variation in amount of developed silver.

Figure 6 shows the spectrophotometric curves of silver obtained by three different means of physical development. Curves 1 and 2 are for development of Carey-Lea-type colloidal silver particles embedded in gelatin. The developer consisted of 0.44 g hydroquinone, 53.3 g sodium sulfite, 2.0 g silver nitrate, in a total of 360 cc of solution. The solution was buffered at pH 8.7 by borax. Curve 3 represents silver obtained by postfixation physical development of the exposed emulsion Coating *A* in a modification of the Lumière and Seyewetz *p*-phenylenediamine physical developer.[5] Curve 4 represents silver obtained by solution-physical development of a coating similar to *B*, but containing only one-fifth the amount of colloidal silver. All of these curves show a pronounced maximum in the region 440–460 mμ.

Electron micrographs of the developed silver show that the particles are compact, with no evidence of



5a 5b

5c 5d

Fig. 5. Electron micrographs of silver developed by the *p*-phenylenediamine–sulfite–KBr solutions. 5a and 5b, development at pH 6.4 for 47 and 195 minutes at 20 C; 5c, pH 7.0 for 45 minutes at 20 C; and 5d, pH 12.0 for 0.5 minutes at 20 C.

filament formation. Figure 7a shows an electron micrograph of the silver corresponding to Curve 2 in Fig. 6. The silver particles for Curve 1 were similar in form but of smaller size. Figure 7b shows the electron micrograph of the silver which produced Curve 3. These particles are much more uniform in size than those which produced Curves 1 and 2, although the absorption curves are quite similar in form. The particle size of the silver which produced Curve 4 is relatively uniform, and much smaller than that shown in Fig. 7b.

Development by Elon Followed by p-Phenylenediamine

The Elon–ascorbic acid surface developers yield a type of development which is very close to pure direct interface development. The low pH *p*-phenylenediamine–sulfite developers, on the other hand, appear to yield purely or predominantly solution-physical development. If this is true, and development of the exposed grains is started in an Elon–ascorbic acid developer, development should continue by the solution-physical mechanism when the film is transferred to a low pH *p*-phenylenediamine–sulfite developer.

Several tests were made to see whether the results agreed with the expectations. A typical result is illustrated by the absorption curves given in Fig. 8 and the electron micrographs in Fig. 9. Exposed film was developed for 21 minutes in the dilute Elon–ascorbic acid–KBr developer at pH 8.4. The spectrum of the developed silver is given by the lowest curve in Fig. 8 (cf. Fig. 1). The silver was definitely filamentary in form, as shown in Fig. 9a. The film was then washed without fixing and transferred to a solution of 0.1 *M* *p*-phenylenediamine dihydro-

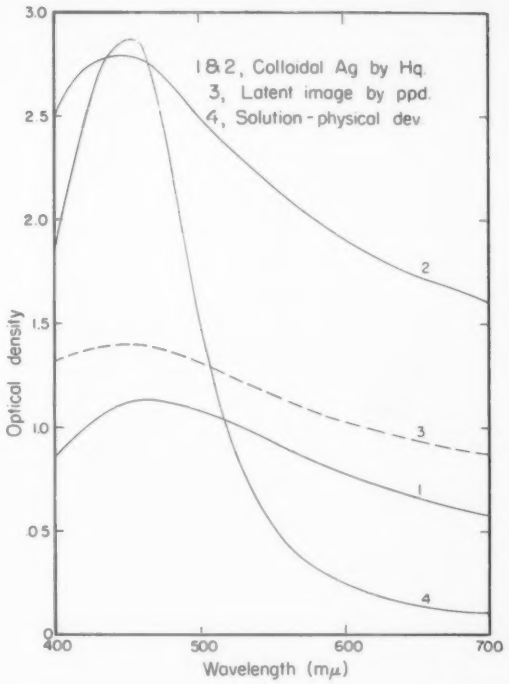
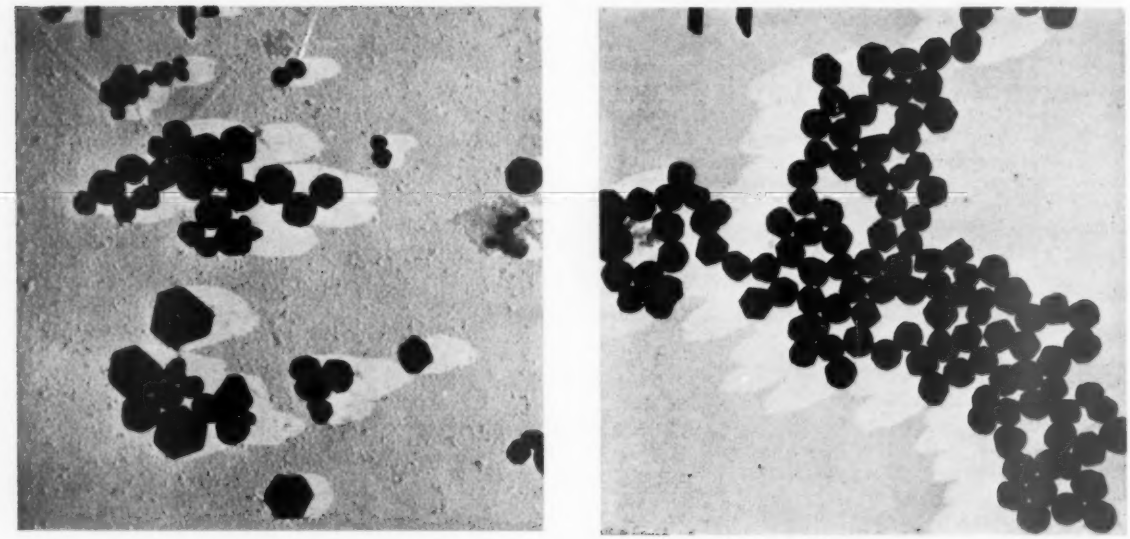


Fig. 6. Spectrophotometric curves for silver produced by physical development. Curves 1 and 2, development of silver sol by a hydroquinone physical developer for 12 and 48 minutes at 20 C. Curve 3, postfixation development of exposed film by a p-phenylenediamine physical developer. Curve 4, solution-physical development of unexposed silver halide onto colloidal silver nuclei.

TABLE V

Development by 0.1 M p-Phenylenediamine Dihydrochloride, 100 Grams Sodium Sulfite, and 1.0 Gram Potassium Bromide per Liter at 20.0 C

pH	Time (min)	D(max)	D(400)	D(700)	Silver mg/sq ft	D(max)/D(700)	D(700)/Ag
6.3	72	0.52	0.41	0.30	39.7	1.73	0.0076
	125	0.72	0.59	0.42	75	1.71	0.0056
	211	0.92	0.79	0.54	126	1.70	0.0043
6.4	47	0.64	0.61	0.37	39.3	1.73	0.0093
	105	1.03	0.85	0.57	104	1.81	0.0055
	135	1.19	1.00	0.66	143	1.80	0.0046
	195	1.39	1.20	0.75	203	1.85	0.0037
7.05	8	0.48	0.39	0.23	20.7	2.09	0.0111
	15	0.82	0.66	0.48	45.3	1.71	0.0106
	26	1.16	0.93	0.64	95	1.81	0.0067
	45	1.47	1.21	0.73	165	2.01	0.0044
8.3	2.5	0.35	0.32	0.16	12.1	2.19	0.0132
	7.5	1.14	0.96	0.63	58	1.87	0.0109
	26	2.19	1.81	1.10	222	1.99	0.0050
	36	2.36	2.03	1.14	276	2.07	0.0041
10.2	2	0.55	0.54	0.23	19.3	2.39	0.0119
	4	1.27	1.20	0.70	62	1.81	0.0113
	7	1.91	1.75	1.18	127	1.62	0.0093
	9	2.15	1.96	1.34	163	1.60	0.0082
12.0	0.11	0.24	0.24	0.18	14.9	1.33	0.0121
	0.25	1.09	1.09	1.00	77	1.09	0.0130
	0.50	2.23	2.22	2.18	164	1.02	0.0133



7a 7b

Fig. 7. Electron micrographs of silver produced by physical development. 7a, silver corresponding to Curve 2, Fig. 6; 7b, silver corresponding to Curve 3, Fig. 6.

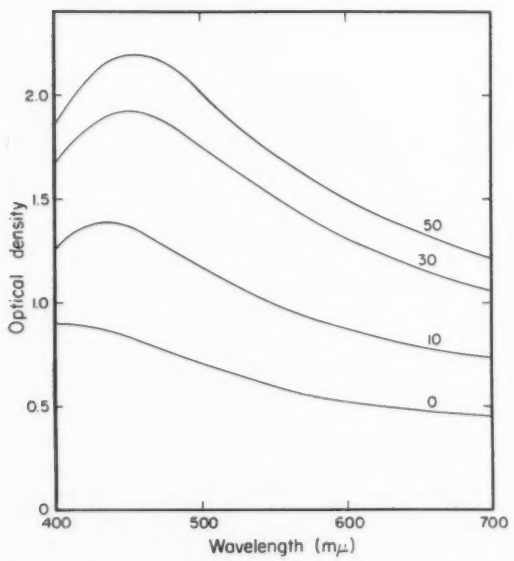


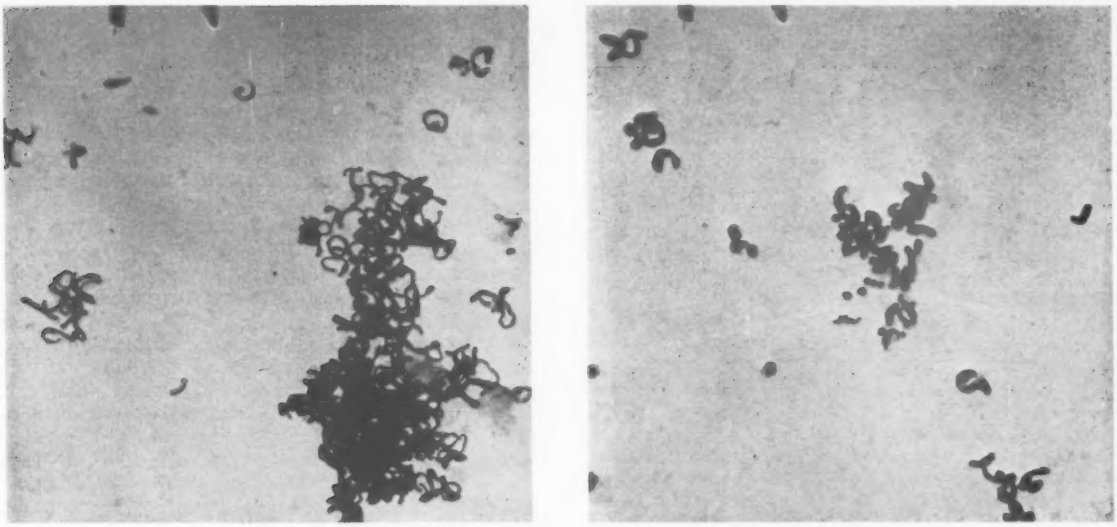
Fig. 8. Spectrophotometric curves for silver produced by development for 21 minutes in the Elon–ascorbic acid–KBr solution of pH 8.4, then for 0, 10, 30, and 50 minutes at 20 C in 0.1M p-phenylenediaminedihydrochloride, 100 g sodium sulfite, and 1 g KBr at pH 6.4.

chloride, 100 g sodium sulfite, and 1.0 g potassium bromide per liter at pH 6.4.

The spectral characteristics of the silver obtained by continued development for 10, 30, and 50 minutes are shown by the upper three curves in Fig. 8. A definite maximum appears at 10 minutes, and the curve for 50 minutes' development closely resembles that obtained by development in the *p*-phenylenediamine solution alone. Figure 9b shows that the appearance of the silver particles after 50 minutes' continued development is similar to that obtained by pure *p*-phenylenediamine development, although most of the particles are oblong instead of round. Similar results were obtained when the continued development was at pH 7.0 and 8.4.

In previous comparisons[6] of the over-all rate of image development with the rate of solution-physical development, it was recognized that the values obtained for solution-physical development onto Carey-Lea silver nuclei could differ considerably from the rates actually operative during development of an exposed grain if the location and the amount of available silver surface for physical development were much different in the two cases. The present results suggest that the differences between the rates are not great.

Figure 10 shows the results of one experiment to test this point. The solid curves represent silver developed as a function of time for development in the *p*-phenylenediamine–sulfite solution alone and for development in that solution after various times of initial development in the Elon–ascorbic acid solution of pH 8.4. The broken curve represents solution-physical development by the *p*-phenylenediamine solution



9a 9b

Fig. 9. Electron micrographs of silver developed in 21 minutes by the Elon–ascorbic acid–KBr solution alone (9a), and followed by 50 minutes a 20 C in the *p*-phenylenediamine solution (9b).

onto the Carey-Lea silver nuclei of Coating *B*. The zero point on the time scale represents the amount of metallic silver present at the start of development by the *p*-phenylenediamine, i.e., silver present as added colloid or developed by the Elon–ascorbic acid developer. The maximum rate of development, as indicated by the slope of the curve, is less than the rate of solution-physical development onto the Carey-Lea nuclei when the exposed material is developed in the *p*-phenylenediamine solution without previous treatment.

When development is initiated in the Elon–ascorbic acid solution for 12 minutes, the rate of subsequent development in the *p*-phenylenediamine solution is nearly equal to the rate of solution-physical development onto the Carey-Lea nuclei. This amount of development in the Elon solution produces compact centers, as shown in Fig. 2a. When development in the Elon solution is prolonged to the point of marked filament formation, corresponding to the upper two curves in Fig. 10, the rate of continued development by *p*-phenylenediamine is somewhat greater than that of solution-physical development onto the Carey-Lea nuclei, but the difference is less than a factor of two.

Other experiments made with *p*-phenylenediamine developers at pH 7.0 and 8.3 gave similar results.

Development by Hydroquinone, Hydroxylamine, and Catechol

A series of tests was made with a developer composed of 0.2 *M* hydroquinone, 100 g sodium sulfite, and 1.0 g potassium bromide per liter. This solution developed very slowly at pH 7.98 and produced a highly colored image. The spectrum of the silver is

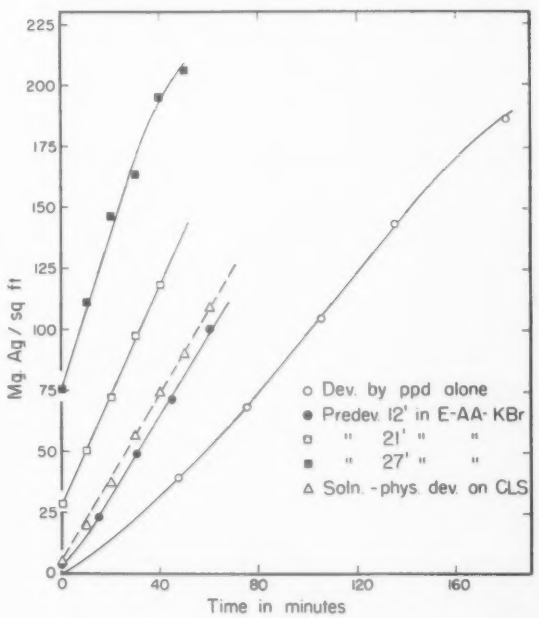


Fig. 10. Rate of image development by 0.1 *M* *p*-phenylenediamine dihydrochloride, 100 g sodium sulfite, and 1 g KBr alone (○), and after predevelopment by Elon–ascorbic acid–KBr for 12 minutes (●), 21 minutes (□), and 27 minutes (■) at 20 C. – – – represents solution-physical development onto colloidal silver.

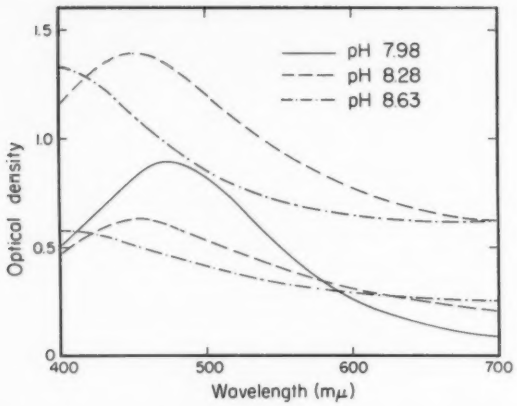


Fig. 11. Spectrophotometric curves for silver developed by 0.2 M hydroquinone, 100 g sodium sulfite, and 1 g KBr. ——— pH 7.98, 420 minutes at 20 C; – – – pH 8.28, 107 and 210 minutes at 20 C; and –·–·– pH 8.63, 29, and 38 minutes at 20 C.

represented by the solid curve in Fig. 11. The character of the silver deposit formed changed as the pH increased, and curves are given for pH 8.28 and 8.63. The dominant mechanism of development evidently changes from solution-physical to direct interface development as the pH increases. At pH 8.63 and above, the characteristics of the silver deposit are similar to those of the silver developed by the Elon solutions. The dependence of the "color ratio" and covering power on the degree of development at pH 8.63 and above likewise resembles that for development by the Elon solutions, whereas at pH 8.28 and below the dependence is similar to that found for the low-pH *p*-phenylenediamine solutions. Numerical data are given in Table VI.

Development which resembles that by Elon is obtained with the hydroquinone solutions of lower pH if an active quaternary salt is added to the developer to increase the rate of direct development. This is shown by the data in the lower part of Table VI. The amount of quaternary salt added was 1.15 g of α-picolinium-β-phenylethyl bromide per liter, and the amount of potassium bromide was decreased to compensate for the bromide of the quaternary salt.

The rate of solution-physical development, as measured for development onto the Carey-Lea silver nuclei, is much less than the total rate of image development by the hydroquinone solution at pH 9.65 (see Table IV). The rate of solution-physical development measured under these conditions is determined by the rate of solution of the silver halide. The relative rates of solution-physical to total development increase as the pH decreases. At pH 8.21, the measured rate of solution-physical development in the absence of quaternary salt is more than five times that of image development over the interval of 10 to 20 per cent reduction of the silver halide. Thus, the latent-image nuclei and the partially developed nuclei must be less efficient in promoting reduction of silver ions than the Carey-Lea nuclei.

This lower efficiency of the latent-image nuclei, even after some development has occurred, may be attributed to their smaller number and, at least in the early stages of development, to the charge-barrier

TABLE VI

Development by 0.2 M Hydroquinone, 100 Grams Sodium Sulfite, and 1.0 Gram Potassium Bromide per Liter at 20.0 C

pH	Time (min)	D(max)	D(400)	D(700)	Silver mg/sq ft	D(max)/D(700)	D(700)/Ag
7.98	210	0.33	0.20	0.01	8.3	33	0.0012
	330	0.67	0.34	0.02	12.5	33	0.0010
	420	0.85	0.46	0.04	16.9	21	0.0024
8.21	70	0.37	0.25	0.04	5.0	6.25	0.0080
	150	1.16	0.96	0.51	31.5	1.88	0.0162
	210	1.72	1.51	0.78	65	1.94	0.0120
	270	2.38	2.21	1.15	98	1.92	0.0117
8.63	29	0.54	0.54	0.22	18.9	2.45	0.0116
	38	1.29	1.29	0.58	48.2	2.22	0.0120
	50	2.44	2.44	1.28	103	1.91	0.0124
9.65	1.25	0.40	0.40	0.20	17.8	2.00	0.0112
	1.50	0.76	0.76	0.45	30.8	1.69	0.0146
	1.75	1.23	1.23	0.82	52	1.50	0.0158
	2.5	2.38	2.38	1.87	116	1.27	0.0161
				Quaternary Salt added			
7.78	16	0.34	0.34	0.14	15.5	2.43	0.0090
	19	0.73	0.73	0.37	31.1	1.97	0.0119
	22	1.28	1.28	0.71	60	1.80	0.0118
	25	1.79	1.79	1.10	89	1.63	0.0124
7.99	7	0.32	0.32	0.16	16.6	2.00	0.0096
	9	0.88	0.88	0.54	43.3	1.63	0.0125
	11	1.61	1.61	1.07	78	1.50	0.0137

effect. At pH 8.21 and below, the rate of solution is not completely rate-controlling for solution-physical development. This is shown by the fact that the measured rate depends on the hydroquinone concentration and also is lower than the rate obtained with Elon at the same pH. The rate of chemical reaction at the silver surface at least partly determines the over-all rate, and the amount of silver surface becomes of much more importance than it is at the higher pH levels. Hence, the rates measured with the Carey-Lea coatings are not directly applicable to image development in this case.

When the exposed film was first partially developed in the Elon–ascorbic acid surface developer until 2 per cent of the total silver halide had been reduced, the rate of continued development in the hydroquinone solution of pH 8.21 was still smaller than that of solution-physical development onto the Carey-Lea nuclei. The initial development by Elon, in this case, yields a mixture of filaments and roughly spherical nuclei. When the initial development was continued until 6.5 per cent of the total silver halide had been reduced, the rate of continued development by the hydroquinone eventually equalled that of solution-physical development onto the Carey-Lea particles. The silver formed by this higher degree of initial development was largely filamentary in character. The filaments evidently are about as effective as the Carey-Lea nuclei in catalyzing the reduction of silver ions at the silver surface.

Some development tests were made with a solution of 0.2 *M* catechol, 100 g sodium sulfite, and 1.0 g potassium bromide per liter over the pH range, 8.5–10.0. The spectrophotometric curves of the silver deposits resembled those obtained with Elon and those obtained with hydroquinone at pH 8.6 and above. The relative importance of solution-physical development decreased as the pH increased, and the changes which occurred in the quantitative form of the curves corresponded to those observed for silver developed by the Elon solutions. Very probably, if the pH were lowered sufficiently, this catechol developer would show the same transition to physical development domination as the hydroquinone developer showed.

Development tests were made with a solution of 0.2 *M* hydroxylamine, 100 g sodium sulfite, and 1.0 g potassium bromide per liter at pH 10.65 and 11.82. The spectrum of the silver formed at the lower pH showed a definite maximum in the visible, and the dependence of the color ratio and covering power on the degree of development was of the same type as observed with the *p*-phenylenediamine developers of low pH. On the other hand, the spectral density curve of the silver formed at pH 11.8 showed no maximum, the color ratio continued to decrease with increasing time of development, and the covering power reached a substantially constant value at a low density. Thus, the character of development by the hydroxylamine–sulfite solution undergoes a change in the pH region, 10.6–11.8, which is similar to that shown by the *p*-phenylenediamine solutions in the same pH range and by the hydroquinone solutions in the pH range, 8.2–8.6.

Absorption of Silver in the Ultraviolet Region

Specular density spectrophotometric curves were obtained over the range, 270–700 mμ, for the filamentary silver developed by hydroxylamine at pH 11.8 and for the compact silver developed by the *p*-phenylenediamine at pH 7.0. Curves for two different times of development in each solution are shown in Fig. 12. Both types of silver deposit show a minimum density at about 320 mμ, but some difference is apparent in the shapes of the curves on each side of the minimum. The maximum specular density for the filamentary deposit lies at 380–400 mμ, and for the brown compact deposit at 480–500 mμ (compared with 450–460 mμ for the maximum integral density).

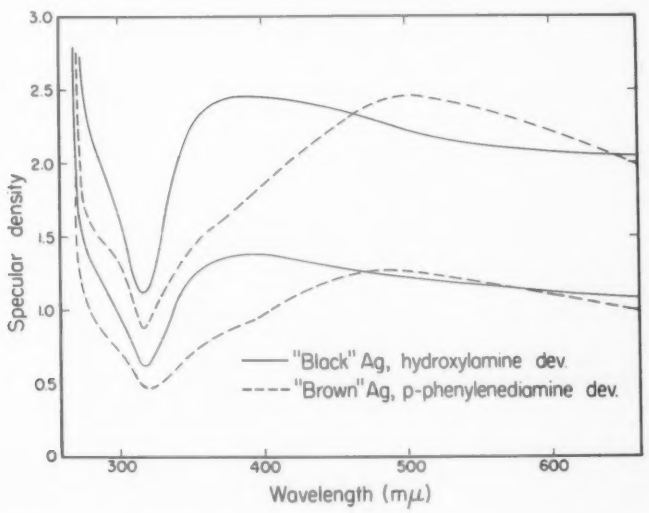


Fig. 12. Comparison of spectral distribution of specular densities of silver produced by a *p*-phenylenediamine–sulfite–KBr solution of pH 7.05 (broken curves) and a hydroxylamine–sulfite–KBr solution of pH 11.8 (solid curves).

Crystal Size Determination

The crystal size* was determined from measurements of x-ray diffraction line-broadening, as previously described.[9] In his previous work, Berry had obtained crystal sizes in the range of 15–20 mμ for silver developed by active solutions, such as Kodak Developers D-8 and D-19, and in the range of 27.5–40 mμ for silver deposited by postfixation physical development. The results obtained on the present samples are listed in Table VII. The values obtained for silver developed by the Elon–ascorbic acid and Elon–sulfite solutions are within the range or slightly above the values previously obtained for D-8 and D-19 development. Those obtained for silver developed by the *p*-phenylenediamine–sulfite solutions are larger and within the range previously found for physical development. The values obtained for silver when development had been started in the Elon–ascorbic acid solution and continued in the *p*-phenylenediamine–sulfite solution are intermediate. In general, the present results agree with those reported by Cassiers,[5] who found that the primary crystallites which made up the blue-black image particles were smaller than those which made up the brown image particles.

TABLE VII
Size of Primary Crystallites Which Make Up the Developed Silver Image Particles

Developer	Relative Amount of Silver	Crystal Size (mμ)
Elon–ascorbic acid, pH 8.4	41	21.2
Elon–sulfite, pH 6.9	51	21.9
Elon–sulfite, pH 7.5	44	23.5
	66	21.3
Elon–sulfite, pH 10.0	49	17.9
	67	18.4
p-Phenylenediamine–sulfite, pH 6.4	44	27.5
	60	26.8
	72	29.1
	84	29.3
Initial, Elon–ascorbic (27′); final, ppd–sulfite	61	26.6
	71	25.3
	83	24.2

Development of a Negative-Type Emulsion

A few tests were made on a silver bromide negative-type emulsion to determine whether the trends observed with the motion-picture positive emulsion held also for an entirely different type. In general, the divergence of the developed silver from spectral neutrality was less for the negative than for the positive type, but the same qualitative dependence of color on the type of development held. In the Elon–sulfite series, the divergence from spectral neutrality increased as the pH decreased and hence as the relative importance of solution-physical development increased. The only qualitative difference observed between the images developed from the exposed positive-type and the exposed negative-type emulsions was in the relation of covering power to degree of development by the surface-type developers. Whereas the covering power measured at 700 mμ was nearly independent of the degree of development for the positive-type emulsion, it decreased with increasing density for the negative-type emulsion. For a given density, however, the covering power of the silver developed by the surface-type developer was still considerably higher than of that developed by the *p*-phenylenediamine–sulfite solutions.

* The crystal size of the silver in some of the developed samples obtained in the present work was determined by C. R. Berry, of these Laboratories.

Discussion

In the present investigation, large changes in the color of the developed silver and in the morphology of the silver grains were obtained simply by varying the pH of the developer or changing the active developing agent. The basic solution contained 100 g sodium sulfite and 1 g potassium bromide per liter. The only other components were the developing agent and either sulfuric acid or sodium hydroxide added to adjust the pH. The photographic material was fully exposed to low-intensity light to insure that substantially all of the grains were developable. Under nearly all of the experimental conditions, except where the rate of development was diffusion-controlled, the increase in density with increase in time of development involved primarily an increase in the degree of reduction of the individual grains rather than an increase in the number of developed grains.

Two distinct types of development can be recognized in the present results. The first type is shown most clearly by the Elon–ascorbic acid developer and the Elon–sulfite developers of higher pH. The second type is shown by the *p*-phenylenediamine–sulfite developers of low pH. These types differ in the morphology of the developed silver, in the variation of image color with degree of development, and in the dependence of covering power upon density.

The characteristics of the first type are shown in Figs. 1 and 2 and in Table II. In the early stages of development, the spectrophotometric density curve shows a maximum in the visible region. The electron micrographs show that the silver particles are very small and are non-filamentary. As development proceeds, the maximum shifts to shorter wavelengths. The curves for the later stages of development show no well-defined maximum in the visible region. This transition in the spectrophotometric density curves accompanies the formation of filaments in the developed silver. As development proceeds, the filaments do not appear to change significantly in size, but become more closely packed, and the spectrophotometric curves approach neutrality. The color ratio of the image, as measured arbitrarily by the ratio of the maximum density (in the 400–700-mμ range) to the density measured at 700 mμ, decreases constantly with increasing degree of development. The covering power for densities measured at

700 mμ increases at first with increasing density, but reaches a maximum at a low density value and subsequently is independent of density (for the positive-type material, but not for the negative). The covering power for densities measured at 400 mμ or at the maximum, of course, would decrease with increasing density in this region.

The characteristics of the second type are shown in Figs. 4 and 5 and in Table V. The spectrophotometric density curves show a maximum for all degrees of development. Except for the early stages of development, the position of this maximum does not change significantly with increasing degree of development, and it is at about 460 mμ (for integral or total density). The silver particles show no sign of filamentary structure at any stage of development, but the particle size increases with increasing degree of development. The particles have a shape roughly similar to a doorknob and a thickness of about one-half to two-thirds the diameter. The ratio of the maximum density to the density measured at 700 mμ decreases to a minimum as development progresses, and subsequently increases. The covering power for densities measured at 700 mμ reaches a maximum at a low density value, and subsequently decreases continuously with increasing density.

The preceding characteristics can be recognized to varying degrees in the images produced by the different developers studied. The type of silver deposit produced, or the relative mixture of the two types, can be correlated with the relative extent to which solution-physical development occurs during the formation of the silver deposit. The rate of solution-physical development by the Elon–ascorbic acid developer is less by two orders of magnitude than the measured rate of image development, and hence plays no significant part in that development. The rate of solution-physical development by the *p*-phenylenediamine–sulfite solutions of low pH is about equal to that of image development, and evidently is the dominant mechanism of development by these solutions.

The Elon–sulfite series demonstrates the effect upon the image characteristics of changes in the relative amount of solution-physical development in a system where direct development predominates. The relative amount of solution-physical development increases as the pH of the solution decreases. At the pH 9.98, the amount of solution-physical development which occurs during normal image development is insignificant. At pH 6.5, it probably does not account for more than 20–30 per cent of the total development in the later stages, and less than that in the early stages. For a constant developed density, the covering power decreases as the relative amount of physical development increases. The color ratio of the image, as measured by the ratio of the density maximum to the density at 700 mμ, increases with increasing relative amount of physical development.

The characteristics of the silver image produced by the hydroquinone developer at pH 9.65, the catechol developer at pH 9.48 and 10.0, and the hydroxylamine developer at pH 11.82 are essentially those of the first type. In all of these developers, the measured rate of image development is much greater than that of solution-physical development. The relative importance of solution-physical development in any of the developer series examined increases with decreasing pH, and the characteristics of the second type of silver deposit become more evident as the pH decreases. Some of the developers show a transition from predominantly Type One to predominantly Type Two images as pH decreases. The hydroquinone and hydroxylamine developers show this transition quite clearly.

The hydroquinone–sulfite solution of pH 8.21 even shows evidence that a transition occurs during the course of development. The image silver produced during the early stages of development is quite clearly of the second type. The spectrophotometric density curves show a definite maximum for all times of development tried, but the maximum shifts towards shorter wavelengths as development proceeds. The covering power decreases rapidly from the maximum for a while, but appears to level off during the later stages of development. Simultaneously, filamentary silver makes its appearance in the image. The hydroxylamine solution at pH 10.65 may represent a transition in the opposite direction. The color ratio appears to approach a minimum which is greater than one as development proceeds, the covering power starts to decrease more rapidly with increasing density, and the maximum in the spectrophotometric density curve shifts towards longer wavelengths.

An explanation can be given for these two cases. In the early stages of development by the hydroquinone, the charge effect greatly restrains direct development and physical development predominates even though the available silver nuclei are small. As development proceeds, the charge effect exerts less restraining action on direct development, and that type becomes relatively more important. Development by hydroxylamine, on the other hand, is not much influenced by the charge effect. The relative importance of physical development increases after a sufficient amount of silver surface becomes available through direct development. The same may be true for the *p*-phenylenediamine–sulfite solutions of low pH. Development by these solutions shows an "induction period" which cannot be attributed to a charge effect. This induction period may represent a stage in which a direct development process forms sufficient silver to allow the solution-physical development process to become dominant.

The characteristics of the image silver discussed above probably appear in a general way for development over a wide range of exposures and development conditions. Some changes are to be expected with change of exposure, and under extreme conditions of development. When the rate of development is controlled by the rate of diffusion, or when the exposure level corresponds to the toe region of characteristic curve, the increase in density with increase in time of development is determined more by an increase in the number of developed grains than by an increase in degree of development of the individual grains. The color ratio for Type One silver images under such

conditions will show less dependence on the time of development. The covering power for Type Two silver images will show less dependence on the time of development. These expectations have been supported by the limited tests which have been made thus far.

Faerman and Shishkina[10] noted that *p*-phenylenediamine (solution composition not given) forms filaments which are thicker and shorter than those obtained with conventional M.-Q. developer, but they found that similar short, thick filaments can be obtained with an M.-Q. developer of high bromide content or with a hydroquinone developer which contains 0.52 to 0.70 mole bromide per liter. They attribute this change to solvent action. Bromide at high concentrations markedly increases the rate of solution of silver bromide, and should increase the relative importance of solution-physical development. The observation of Küster,[11] that thicker filaments were obtained with Agfa 20 developer diluted 64-fold than with the same developer diluted 16-fold, can be explained on the same basis, since the *relative* rate of solution-physical development would be greater in the more dilute solution. Levenson and Tabor[12] found that a transition from filament formation to platelet growth occurred when the net rate of development in an iron salt developer was sufficiently slowed down by adjustment of the redox potential. Relative rate data are not available for solution-physical development and over-all development in the solutions used, but it seems quite probable that the solvent action of water would be sufficient to permit a large amount of solution-physical development to occur in the long times of development used to obtain the platelet formation. There is no such thing as a truly nonsolvent aqueous developer. The results obtained by Levenson and Tabor, however, may also be related to the fact that they used a reversible developer, and oxidation and reduction of silver would occur simultaneously.

References

1. Mees, C. E. K., *The Theory of the Photographic Process*, 1st ed., pp. 562–8. The Macmillan Co., New York (1942). *See also* Pinoir, R., Thornton, E., and Baby, P., *Science and Applications of Photography*, p. 196. The Royal Photographic Society, London (1955).
2. Wiegel, E., *Z. Physik*, Vol. 136, p. 642 (1954).
3. Mees, *op. cit.*, p. 568; see also rev. ed. (1954), pp. 755–7.
4. Koerber, W., *Sci. et inds. phot.* (2), Vol. 27, p. 475 (1956).
5. Cassiers, P. M., *Sci. et inds. phot.* (2), Vol. 28, p. 36 (1957).
6. James, T. H., and Vanselow, W., *Phot. Sci. Tech.*, Vol. 2, p. 135 (1955); *Phot. Eng.*, Vol. 7, p. 90 (1956).
7. James, T. H., *Phot. Sci. Tech.*, Vol. 2, p. 81 (1955).
8. Fortmiller, L. J., James, T. H., Quirk, R. F., and Vanselow, W., *J. Opt. Soc. Am.*, Vol. 40, p. 487 (1950).
9. Berry, C. R., *Sci. et inds. phot.* (2), Vol. 27, p. 474 (1956).
10. Faerman, G. P., and Shishkina, N. N., *J. Appl. Chem. U.S.S.R.*, Vol. 25, p. 857 (1952); *Zhur. Priklad. Khim.*, Vol. 25, p. 776 (1952).
11. Küster, A., *Z. wiss. Phot.*, Vol. 43, p. 191 (1949).
12. Levenson, G. I. P., and Tabor, Joan H., *Sci. et inds. phot.* (2), Vol. 23, p. 295 (1952).

PHOTOGRAPHIC SCIENCE AND ENGINEERING
Volume 1, Number 3, January 1958

Some Properties of Developer Fog

R. W. SWENSON, *Photo Products Department*,
E. I. du Pont de Nemours & Co., Inc., Parlin, N.J.

During development, fog formation in photographic emulsions occurs in two stages. The first stage — emulsion fog — develops rapidly to its maximum, whereas the second stage — developer fog — has a long induction period and develops slowly.

Emulsion fog can be caused by excessive chemical sensitization and unintentional light exposure, as well as by normal and accelerated aging processes. None of these factors influence developer fog. Emulsion fog can be destroyed before development by mild oxidizing agents without affecting subsequent developer fog. The development rate and the covering power of the developed silver for emulsion fog are approximately the same as for exposed image.

Developer fog is characterized by the high temperature coefficient of the reaction rate and the low covering power of the developed fog silver. Developer fog is unaffected by many environmental factors, but can be accelerated by certain optical sensitizing dyes. In a metol-hydroquinone developer, the formation of developer fog increases with increasing pH.

The formation of fog during processing can arise from many different causes, both in the emulsion and in the developer. Descriptive names such as "dichroic fog" and names implying the cause, such as "aerial fog," were summarized by Dundon and Crabtree[1] and have been widely used for many years. James[2] divided fog reactions into "catalyzed" and "non-catalyzed" categories and showed that the former resembles the development of the latent image.

The Sequence of Fog Formation

The two general stages of fog formation can be demonstrated in a single emulsion. Under some circumstances, such as high-temperature rapid processing, both stages assume practical importance in the fog level of a processed emulsion. The fog which appears first during development is designated "emulsion fog" and is the catalyzed variety. The secondary fog or "developer fog," occurs more slowly after a long induction time. Figure 1 gives an example of this simple sequence of fog formation in an experimental coarse-grain blue-sensitive bromo-iodide emulsion. The developer was a simple metol-hydroquinone developer of the following composition:

Component	Quantity in grams
Metol	3.0
Hydroquinone	9.0
Sodium sulfite, anhydrous	50.0
Potassium carbonate, anhydrous	50.0
Potassium bromide	4.5
Water to make 1 liter	

Presented at the Annual Conference, Asbury Park, N.J., 12 September 1957. Received 9 September 1957.

In the example in Fig. 1, normal image development required about 4 minutes and was substantially complete before secondary developer fog became serious.

Classifications of Fog

Emulsion fog is caused most often by excessive chemical sensitization or "digestion" during the manufacturing process and by shelf aging processes, both normal and accelerated by high temperature and humidity. Chibisov and Mikhailova[3] have discussed chemical fog, and aging processes have been investigated by Smith.[4]

James[5] has shown that aerial fog results from oxidation processes primarily in the developer, but its properties are the same as emulsion fog. Emulsion

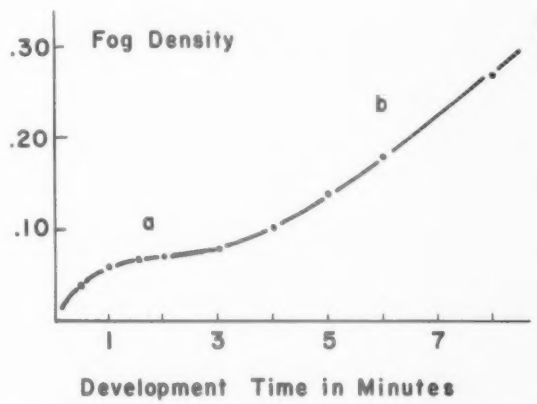


Fig. 1. Typical sequence of fog formation during development. Part a of curve — Emulsion Fog; Part b — Developer Fog.

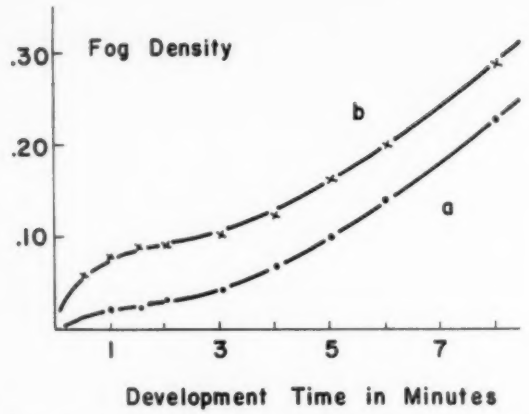


Fig. 2. Curve a — fog sequence in an emulsion with very low emulsion fog; Curve b — same emulsion after accelerated aging.

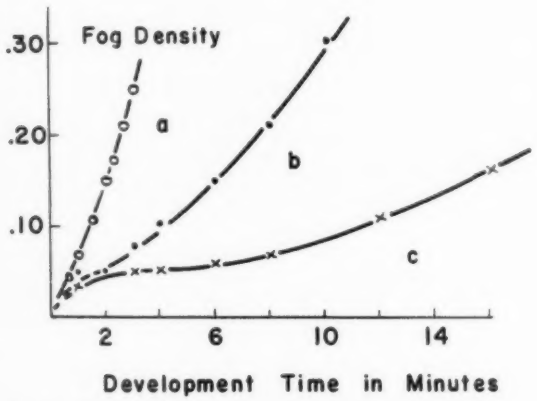


Fig. 3. Effect of developer temperature on fog sequence in same emulsion. Curve a — 80 F; Curve b — 68 F; Curve c — 59 F.

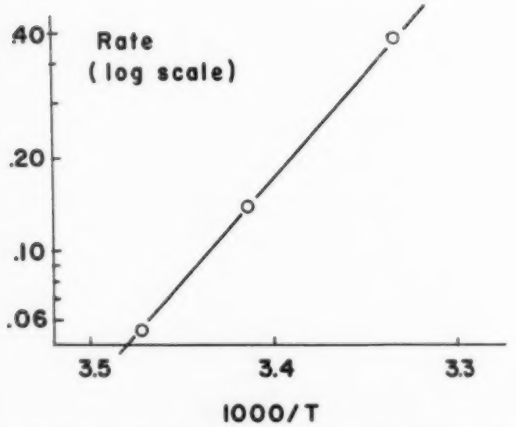


Fig. 4. Temperature dependence of developer fog formation (1/t rates). Experimental energy of activation: 28 kcal/mole.

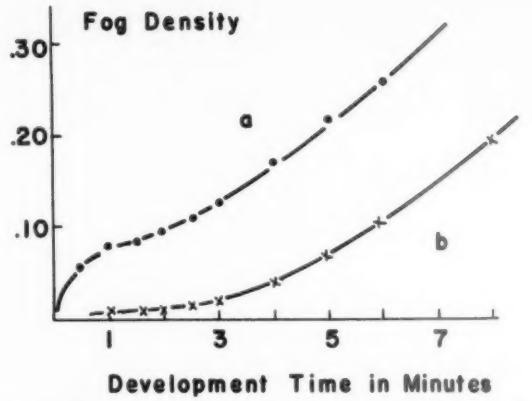


Fig. 5. Curve a — fog formation in an emulsion with relatively high emulsion fog; Curve b — fog formation in the same emulsion following a 2-minute bleach.

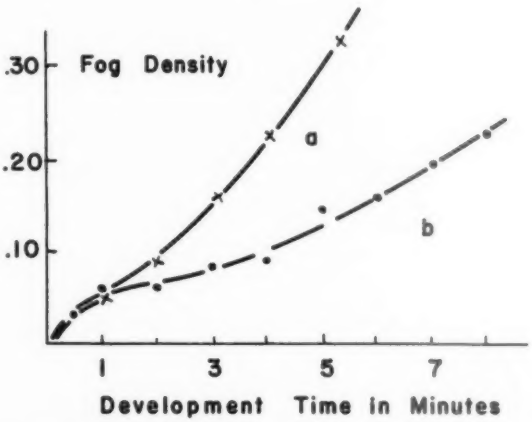


Fig. 6. The effect of certain dyes on developer fog formation. Curve a — fog curve for an emulsion optically sensitized with 3,3′-diethyl-9-methylthiocarbocyanine; Curve b — same emulsion with 5-5′dibromo-3-3′diethyl-9-methylthiocarbocyanine.

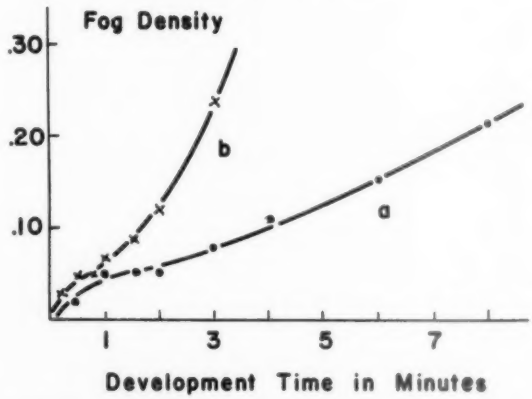


Fig. 7. The effect of developer pH on developer fog formation. Curve a — pH = 10.4; Curve b — pH = 12.0.

fog must also include light fog, which is a non-intentional latent image. The similarities between fog produced by light and fog produced by chemical means re-emphasize the similarities between the various forms of latent emulsion fog and latent image.

Developer fog is a nonselective reduction of silver halide to silver by the developing agent. "Dichroic" fog[6] belongs to this category.

The Independent Nature of Developer Fog

Secondary developer fog usually is unaffected by the level of emulsion fog. In Fig. 2, the sequence of fog formation is plotted for two emulsions having different emulsion fog levels. The higher emulsion fog level was induced by accelerated aging. It is evident that the secondary developer fog is the same in both cases. If the emulsion fog "plateau" were subtracted from both curves they would coincide.

Development of Emulsion and Developer Fog

Development Rate and Temperature Dependence

The rate and the temperature dependence of the emulsion fog and developer fog reactions are characteristically different. From Figs. 1 and 2 it can be seen that the developer fog reaction has a longer induction time and lower rate than the emulsion fog reaction. James[2] has shown that both the induction time and development rate of emulsion fog resemble those observed in the development of a latent image.

The temperature dependence of secondary developer fog formation is very much greater than that for the primary level of emulsion fog. In Fig. 3 the sequence of emulsion and developer fog is illustrated for the same emulsion at three temperatures from 56 F to 80 F. It should be noted that the emulsion fog plateau is unaffected by temperature. Table I lists rates of secondary developer fog formation for the three temperatures based on 1/t where t is the time in minutes to reach a fog density of 0.20.

TABLE I

Temperature	Rate (1/t)	Temperature Coefficient	
59 F (15 C)	.055	(1/F)	(1/C)
68 F (20 C)	.139	.28	.51
80 F (26.7 C)	.384	.23	.41

The temperature dependence of developer fog formation can be described by the Arrhenius equation:

$$v = A_o^{-E_a/RT}$$

where E_a is the experimental energy of activation, v is the rate of developer fog formation, A is a constant, R is the gas constant, and T is the absolute temperature. This can be demonstrated by a plot of log v vs. 1/T, such as shown in Fig. 4 for the data of Table I. Under these circumstances E_a has a value of about 28 kcal/mole. The energy of activation for emulsion fog development is much lower, being close to that of image development,[2] and for this combination of emulsion and developer is only 8 to 10 kcal/mole (a temperature coefficient of approximately 0.12 (1/F) from 68 F to 80 F). These data need not be amplified here.

From a practical point of view, high temperature processing will necessarily involve the risk of higher developer fog since an increase in temperature will increase the developer fog reaction rate relatively more than the image rate.

The Effect of Bleach on Emulsion and Developer Fog

A bleach solution will remove latent emulsion fog without affecting subsequent developer fog. A suitable bleach for demonstrating this property of emulsion fog is 0.1 per cent potassium ferricyanide in an acetic acid-sodium acetate buffer.[7] In Fig. 5, which illustrates the effect of bleach on accelerated aging fog, a 2-minute bleach has removed almost all traces of emulsion fog but has not changed the onset or slope of developer fog formation.

The bleaching properties of emulsion fog are further evidence of the basic similarities between latent emulsion fog and a normal latent image. The bleach susceptibility of surface sensitivity such as discussed recently by Dyba and Smith[8] is at least as great as the bleach susceptibility of the emulsion fog. For practical photographic purposes, latent emulsion fog cannot be removed by bleaching without destroying sensitivity.

The Effect of Some Optical Sensitizing Dyes on Fog

Optical sensitizing dyes sometimes contribute to fog. Natanson[9] has shown that carbocyanine dyes which increase fog form a complex with silver ion and that noncomplexing dyes are nonfogging. As an interesting supplement to this work it has been found that the fog formed by these complexing dyes is developer fog and not emulsion fog. This is one of the few emulsion factors which materially affect developer fog. Developer component effects on developer fog have been discussed by James.[2]

The effect of a typical carbocyanine dye, 3-3′-diethyl-9-methylthiocarbocyanine, on developer fog is illustrated in Fig. 6. It is compared with a related dye which has no effect on developer fog, 5-5′dibromo-3-3′diethyl 9-methylthiocarbocyanine. These two dyes were used in equal concentration and were added before coating to separate portions of the same type of experimental emulsion used to illustrate other fog effects. Titration of these dyes with neutral silver nitrate revealed that the former will complex with silver ion but not the latter.

Experiments made at different temperatures similar to those illustrated in Fig. 3 showed that the fogging dye did not influence the temperature coefficient of the developer fog reaction. Therefore, while certain dyes of this type increase the rate of developer fogging they presumably do not change the experimental energy of activation or the fundamental mechanism of the reaction.

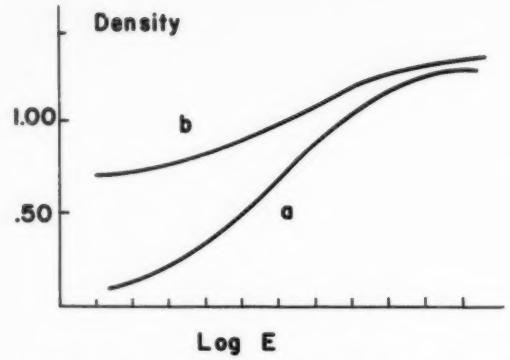


Fig. 8. Complete reduction of silver halide to silver by prolonged development. H & D curves derived from film samples developed for 4 minutes (Curve a); for 16 hours (Curve b).

The Effect of Emulsion pH and pAg and Developer pH

Emulsion pH and pAg (the hydrogen ion and silver ion concentration at coating) affect a wide variety of photographic properties,[10] but these chemical factors do not influence emulsion or developer fog. It is known, however, that these factors will affect aging fog[11] and in this sense emulsion pH and pAg influence emulsion fog indirectly.

An increase in pH increases developer fog with a hydroquinone[2] developer and the same phenomenon can be demonstrated in a metol-hydroquinone developer of the composition noted above. In Fig. 7, developer fog is related to developing time for the same emulsion when developed in the same developer at pH 10.4 and pH 12.0. The temperature coefficient is smaller at pH 12.0 than at pH 10.4 (see above) and the activation energy is about 19 kcal/mole compared with about 28 kcal/mole at the lower pH. Fortmiller and James[12] have accounted for similar reductions in activation energy in terms of heats of ionization of hydroquinone.

Properties of Developed Fog

Covering Power of Emulsion and Developer Fog

The covering power of developer fog silver is very low[7] but the covering power of emulsion fog silver is relatively high and about the same as that of image silver. For a fog sequence such as illustrated in Fig. 1, the emulsion fog "plateau" has a covering power of about 22 (D/g Ag dcm^2) while the developer fog (e.g., D = .20) has a net covering power of only 12.

This fundamental difference in covering power may be illustrated by gross overdevelopment to the point where all silver halide is reduced to silver, regardless of exposure. A typical result is illustrated by the H & D curve in Fig. 8. The toe of this curve represents almost entirely developer fog silver with a covering power of 13, the shoulder represents entirely image silver with a covering power of 23. The mass of silver is exactly the same in both toe and shoulder regions. This difference in covering power sometimes permits printing of a negative which accidentally has been overdeveloped.

Microscopic and Macroscopic Appearance of Emulsion and Developer Fog

Developer fog silver appears a light dull brown

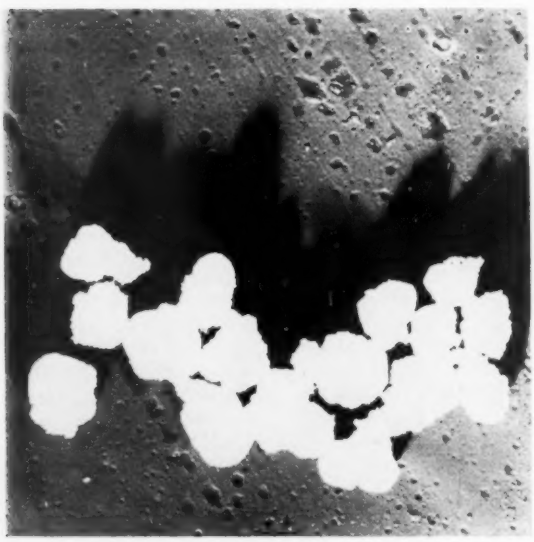


Fig. 9a. Electronmicrograph showing typical large crystalline chunks of developer fog silver. The chromium shadowing gives an indication of the vertical dimensions.

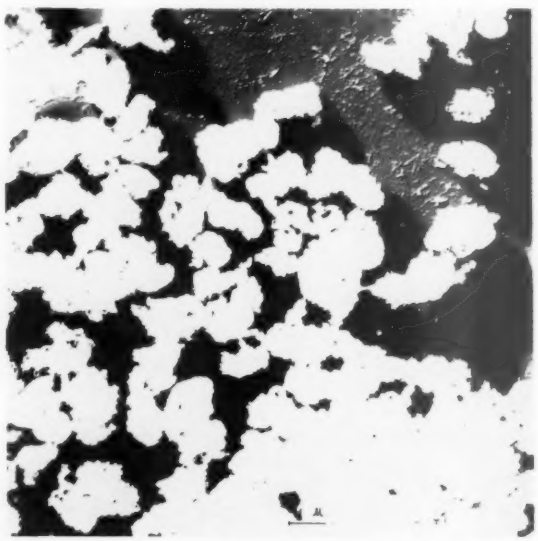


Fig. 9b. Electronmicrograph showing a mass of tangled smaller grains typical of image silver (and emulsion fog). Greater magnification would show more of the filamentary structure.

compared with the cold black of image or emulsion fog silver. In the electron microscope, developer fog is seen to consist of massive chunks of crystalline silver, but image or emulsion fog appears as smaller tangled masses of silver (Figs. 9a and 9b.) Hall and Schoen[13] have shown that the massive crystalline chunks of silver are typical of "physical" development and the smaller tangled masses of chemical development.

Bleach experiments on image and developer fog reveal a much slower rate of bleaching for developer fog. This indicates a smaller surface to mass ratio for developer fog and is in good agreement with the microscopic evidence. X-ray diffraction data, however, do not show significant differences in the crystal habit of developer fog or image and emulsion fog.

Discussion

The differences in formation and properties of emulsion and developer fog clearly suggest basic differences in mechanisms. James[2] has suggested that formation of emulsion fog is a fast, "catalyzed" reaction similar to image development while developer fog results from a slower, nonselective, noncatalyzed, "physical" type reduction.

It is important to note that, in addition to being nonselective or noncatalyzed, developer fog *remains* developer fog during development even if the reduction of all the silver halide in the emulsion is carried to completion (Fig. 8). The low covering power of developer fog remains low rather than slowly approaching the covering power of image or emulsion fog silver. This implies that developer fog neither starts nor continues on a grain, but is external to the grain; otherwise, the silver formed by the reaction might be expected to behave similarly to a latent image and start a "catalyzed" reaction.

The influence of silver complexing dyes on developer fog is interesting in regard to the developer fog mechanism. Although sensitizing dyes are usually adsorbed to silver halides, it appears likely that a silver-dye complex might not be. During titration these complexes cloud the solution and frequently precipitate. Such an insoluble silver-dye complex may be a suitable site for "physical" reduction. Perhaps similar complexes between silver ion and other components of the emulsion, such as gelatin, are reaction sites for the more usual forms of developer fog.

Acknowledgments

The writer is grateful to Rowland Van Cleef for the electron micrographs reproduced as Figs. 9a and 9b. The writer also wishes to acknowledge helpful discussions with Dr. T. D. Smith and other colleagues in these Laboratories.

References

1. Dundon, M. L., and Crabtree, J. L., *Am. Phot.*, vol. 18, p. 7 (1924).
2. James, T. H., *J. Franklin Inst.*, Vol. 234, p. 371 (1942).
3. Chibisov, K. V., and Mikhailova, A. A., *Kino-foto-Khim.*, Vol. 6, p. 24 (1940).
4. Smith, T. D., *J. Phot. Sci.*, Vol. 1, p. 138 (1953).
5. James, T. H., *J. Phot. Soc. Am.*, Vol. 9, p. 390 (1943).
6. Lumière, A. and L., and Seyewetz, A., *Phot. J.*, Vol. 43, p. 223 (1903).
7. Sheppard, S. E., and Ballard, A., *J. Franklin Inst.*, Vol. 205, p. 657 (1928).
8. Dyba, R. V., and Smith, T. D., *Phot. Eng.*, Vol. 7, 98 (1956).
9. Natanson, S., *Acta Physiochim. URSS*, Vol. 21, p. 430 (1946).
10. Swenson, R. W., Forsgard, F. C., and Dyba, R. V., *Phot. Sci. and Tech.*, Vol. 3, p. 162 (1956).
11. Carroll, B. H., Hubbard, D., and Kretchman, C. M., *Bur. Stan. J. Res.*, Vol. 12, p. 223 (1934).
12. Fortmiller, L. J., and James, T. H., *Phot. Sci. and Dev.*, Vol. 18B, p. 76 (1952).
13. Hall, C. E., and Schoen, A. L., *J. Opt. Soc. Am.*, Vol. 31, p. 281 (1941).

PHOTOGRAPHIC SCIENCE AND ENGINEERING
Volume 1, Number 3, January 1958

Internal Camera Vibrations and Their Effect on Resolution

JOHN W. HEROLD, *Squadron Leader (Royal Air Force Exchange Officer)*,
Wright Air Development Center, United States Air Force,
Wright-Patterson Air Force Base, Ohio

Vibrations induced by the internal mechanism of an aerial camera can degrade aerial photographic images. Flight tests conducted under controlled conditions at Wright Air Development Center, Wright-Patterson Air Force Base, with an Air Force aerial reconnaissance camera yielded performance values well below those obtained with the same camera-lens-film combination under laboratory static conditions. Subsequent laboratory tests showed that this limitation was due entirely to internal camera vibrations. The study indicates that a vibration-free camera is essential if stringent photographic requirements are to be met.

The purpose of photographic reconnaissance is to obtain and record information for eventual extraction by photographic interpreters. The ultimate value of the interpretation is dependent on both the quality of the photograph and the skill of the interpreter.

The progress in military aviation since World War II has made it essential for both the Air Force and the aerial camera industry to reappraise the general problem of improving photographic performance. This performance must be continually raised if the Air Force is to increase or even maintain the level of intelligence extraction required by the ever-changing pattern of warfare.

This paper is concerned with only one of the many factors which can impair the photographic image—vibration. A practical study conducted at Wright Air Development Center to evaluate the detrimental effect of vibration on the photographic image was concerned not only with airframe vibrations but, more important at this stage, with the vibrations from the internal mechanism of the camera during operation. The tests were conducted in the laboratory and the laboratory findings were then checked by practical aerial photography. The study is not yet completed but there is already sufficient evidence to justify a review of results obtained to date.

The Study Program

The main purpose was to determine the mechanical deficiencies of the standard Air Force aerial camera by measuring the performance losses caused by the vibrations induced by the dynamics of the system during exposure. It was not possible to determine beforehand how such a program was to be planned in detail, or, in fact, if any constructive conclusions would be forthcoming.

The static performance, or resolution performance, of the camera at rest on an optical test bench should be well in excess of the original specification limit of the system chosen for the study. The higher the static resolution the longer, and hence the more critical, the yardstick from which to judge system performance. The static resolution of the camera was therefore boosted by tightening the mating tolerances and incorporating a known high-performance lens which was used in conjunction with aerial films having finer grain than those normally used for aerial photography. The full optical performance of the camera over the diagonal of the format field at each aperture, and with each type of film to be used during the study, was evaluated.

The system was then flight tested under controlled conditions and any significant resolution losses over those obtained in the laboratory were investigated. The internal causes of the performance loss were eliminated where possible and the system again flight tested under controlled conditions. The results were then analyzed to determine if the performance had been improved by the elimination of the postulated causes. The study was to progress in this fashion until all known limitations were eliminated.

Phase I — Selection of Equipment and Film

Equipment

The selected photographic equipment was representative of standard Air Force equipment or equipment designed for general service. It included:

Camera Body	Type K-17C
Lens	Pacific Optical F/L 24 inches *f*/6 (prototype)

Presented at the Annual Conference, Asbury Park, N.J., 11 September 1957. Received 3 September 1957.

Magazines	Type A-18 (IMC)
Camera Mount	Type LS-6 Torquer Vertical Stabilized
Camera Mount Isolators	Johnsons Type 210-65L
Controls	Type C-4 Control and Type LA-30 (Amplifier)
Filter	Class III Minus Blue (Specification MIL-F-9329 USAF)
Camera Window	Group B (Specification MIL-G-1366C USAF); specially selected and tested prior to study

All tolerances, on both the camera body and the shutter unit, were calculated, and excessive tolerances removed. Shutter speeds were checked and found to be as follows:

Shutter Speed Setting	Actual Shutter Speed
1/50th second	1/40th second
1/100th second	1/127th second
1/150th second	1/127th second

One magazine was selected for use with each film to be flown after tolerances and platen parallelism were found satisfactory. The control and amplifier were calibrated with each magazine and adjusted to provide greatest accuracy over the limited range of heights and ground speeds at which the equipment was to be flight tested.

A torquer development prototype of the Air Force Type A-28 mount was chosen because it was the most advanced design of a vertically stabilized camera platform available.

Films and Processing

Since it was desirable to boost static resolution in order that losses caused by the dynamics of the system could be more easily determined and measured, films capable of high resolution were selected. Kodak Super XX Reconnaissance Base Aerial Film was selected as a standard. It was hoped also early in the study that the information-gathering properties of these films could be evaluated from the flight test results, but, unfortunately, during Phases III and V resolution was not high enough to reveal their full capabilities.

1. Type 1B, Class L Kodak Super XX Reconnaissance Base Aerial Film. Emulsion No. 86-221-42
2. Kodak SO-1121 Aerial Film (Experimental). Emulsion No. SO-1121-35-3
3. Kodak Panatomic X Aerial Film (Experimental). Emulsion No. FE-42737-1
4. Ilford Pan F Aerial Film. Emulsion No. BX 5RA555

All films exposed in the laboratory and in the air were processed at 68 F in a Type B-5 processor with D-19 developer to a gamma of 1.5.

Phase II — Optics Testing

Conventional procedures were followed during the optics testing program which was carried out with each of the films except Ilford Pan F (not then available but tested later).

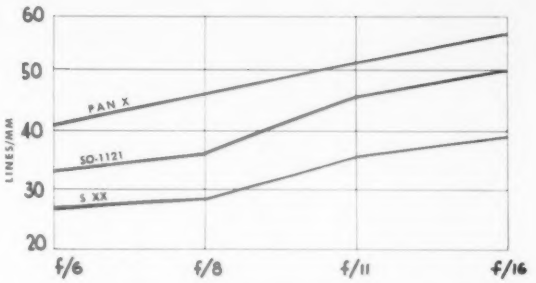


Fig. 1. High contrast A.W.A.R. and aperture efficiency. K-17 camera fitted with F/L 24-inch f/6 Pacific Optical lens. Developed in D.19 to gamma 1.5.

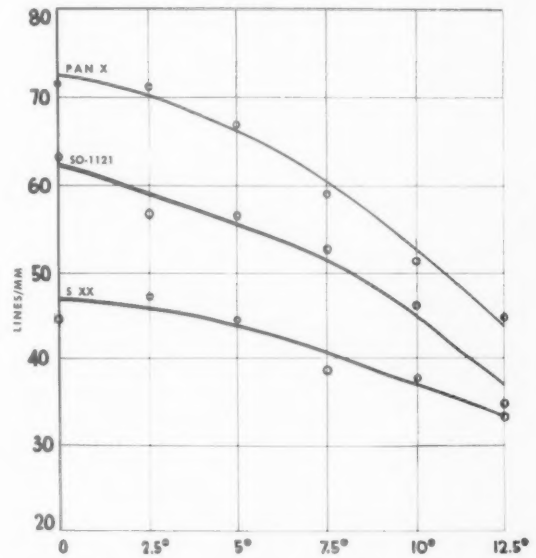


Fig. 2. Film/lens static resolution at most efficient aperture (f/16) across one-half field angle.

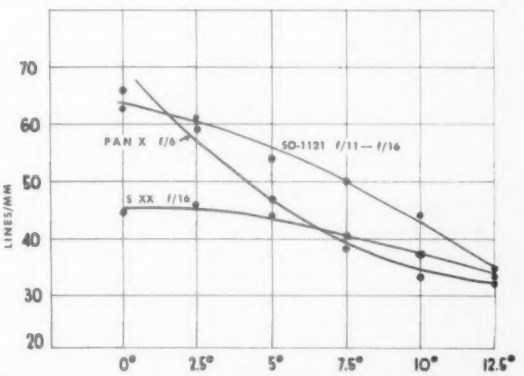


Fig. 3. Resolution vs. field angle obtained for various films at the lens apertures used.

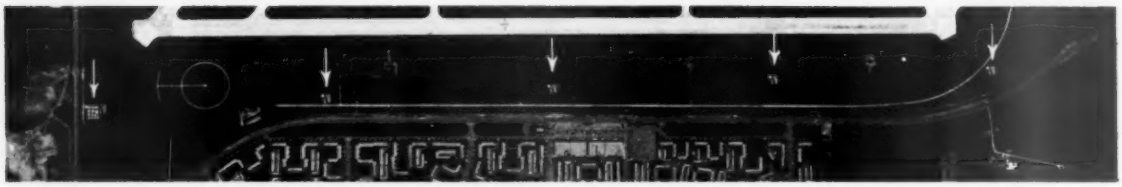


Fig. 4. Five high-contrast resolution targets—Wright Air Development Center, WPAFB, Ohio.

The lens was installed in the camera and further tests made to determine what, if any, high-contrast resolution losses could be attributed to the filter, to the aircraft window and to any other components in the camera system assembled as a unit. All the tests confirmed that there were no resolution losses on any part of the format diagonal. Figures 1, 2, and 3 show the high-contrast resolution capabilities of the complete camera, the filter, and the window in the static state.

Phase III — Flight Trials

A C-47 aircraft was selected for the flight testing because it fulfilled the following requirements, essential for the accomplishment of the photographic missions:

1. The photographic equipment could be installed without any major aircraft modifications.
2. The camera operator could control the equipment personally from an adjacent position.
3. The environmental conditions in the aircraft during flight were not likely to add to the various in-flight factors which might degrade resolution.
4. The aircraft was capable of flying efficiently at 7,000 and 14,000 feet, the heights at which photography would be undertaken.

Since it was anticipated that the flight test program might be carried out over a long period of time, it was necessary to attempt standardization of conditions under which all photography was to be undertaken. It was decided that all photographs were to be made over a common flight path 7 miles long, which included the five high-contrast resolution targets at Wright Field (Fig. 4), and that the heights of 7,000 and 14,000 feet would be accurately determined over the resolution targets. No photography would be undertaken unless the slant visibility from 7,000 feet exceeded 20 miles, nor unless the sun were unobscured. All photography would be carried out between 1130 and 1400 EST. Suitable engine manifold pressure and propeller settings were to be found at 7,000 and 14,000 feet, and these settings used during photography to guard against possible detrimental effects of airframe vibrations on resolution. The in-flight calculations of the height and ground speed (for image movement compensation) were to be of the highest accuracy at all times.

Twenty-three photographic runs were flown during June 1956, utilizing each type of film at shutter speeds of both 1/40th and 1/127th second, and the following conclusions were made after detailed interpretation and resolution target reading:

1. All films, regardless of their emulsion characteristics, the shutter speeds and lens apertures used, and flight altitude, yielded an average high-contrast resolution of approximately 22 lines per mm.
2. There were unsharp areas on some of the negatives which indicated that the film was not always lying flat on the magazine suction platen during the exposure. Two magazines were responsible for this defect and they were discarded.
3. There was little or no indication of incorrect image movement compensation (IMC) at the resolution level reached.
4. The smearing effect of shutter shock and vibration was clearly evident in the images of the resolution targets recorded on the films.

The flight tests indicated beyond all doubt that shocks and vibrations were restricting resolution to a relatively low level regardless of the operating conditions. Since vibration can be generated by the airframe and the camera equipment, it had to be determined if one or both of these sources were responsible for the degradation.

Phase IV — Laboratory Tests — Internal Vibrations Analysis

The object of this test phase was to determine the resolution losses which could be directly attributed to the internal vibrations generated within the camera and mount during the exposing period. If possible, a quantitative analysis in terms of high contrast resolution was to be obtained of the effect on resolution of the operation of each of the mechanical components within the camera.

The entire camera equipment was removed from the aircraft and placed on a rigid stand over a vertical collimator. The equipment was preflight balanced and checked in the normal way, then positioned so that the resolution target projected by the collimator fell directly on the center of the format.

The magazine was loaded with Ilford Pan F film and the collimator lighting regulated to give a suitable negative of the test target at an exposure of 1/127th second at $f/11$.

The static lens/film axial resolution at this aperture was previously calculated during Phase II at 71 lines per mm. This was checked again to confirm the performance of the camera.

The only operating component of the system during the first test was the magazine motor. The camera shutter was opened and inoperative and the mount gyros caged. A series of separate exposures were made, using a collimator stroboflash, calculated at approximately 1/100th second. An average resolution of 48 lines per mm was obtained.

The camera mount was then energized and the test repeated. The average resolution fell from 48 to 45 lines per mm. It was suspected that the camera mount weight shift balance motors might be transmitting a vibration to the camera. When these motors were rendered inoperative, the average resolution returned to 48 lines per mm, indicating that the combination of magazine and weight shift motors were restricting the system performance to 45 lines.

The last series of tests involved the normal operation of the camera, with shutter operating at $^1/_{127}$th and $^1/_{40}$th second, and with the mount in operation and inoperative. Exposures were made in the normal way with target illumination provided by the collimator constant light source. Results of these tests were as follows:

Shutter speed $^1/_{127}$th second, mount inoperative—32 lines per mm
Shutter speed $^1/_{127}$th second, mount operating—33 lines per mm
Shutter speed $^1/_{40}$th second, mount inoperative—33 lines per mm
Shutter speed $^1/_{40}$th second, mount operating—34 lines per mm

It was not possible to determine the losses in resolution attributable to the physical movement of the film platen during the use of IMC. This test would have required a target moving at a constant and known speed across the format during exposure. Traces of the vibrations generated by the film platen mechanism were later produced; they showed almost a 50 per cent increase in vibration amplitude over that of the magazine motor. This indicated that the magazine, in full operation, would probably limit the system performance to less than 48 lines per mm obtained in the collimator tests. Figure 5 illustrates the large reduction in camera performance attributable to the factors already described.

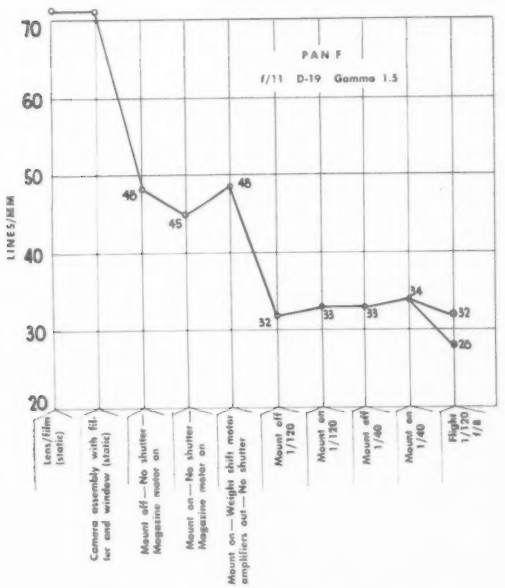


Fig. 5. The effect of mechanical factors on resolution.

No further tests were made because the limiting factors of the system were now known and the various components (except IMC mode) which caused resolution losses had been pinpointed. The following conclusions were drawn from these tests:

1. The camera and mount combination was limited to a maximum of 32 lines per mm high-contrast resolution, regardless of the type of film used.
2. Shutter shock and vibration were the main factors responsible for limiting the performance.
3. There appeared to be little or no variation in the characteristics of the shocks and vibration generated by the shutter unit or shutter motor which, for the purposes of the tests, were treated as one item. The reasonably constant resolution obtained at the two shutter speeds confirmed this finding.
4. It was possible that the movement of the film platen, in addition to the magazine motor movement, would limit resolution below the level of 48 lines per mm.

During this test phase, it was noticed that the vibration isolators, which prevent aircraft vibrations from being transmitted to the mount and camera, were crushed and distorted. Continuous application of an excessive load was the assumed cause of this damage. The isolators were replaced and care was taken thereafter to relieve the weight from them except during use.

Phase V — Flight Trials

An additional fourteen photographic runs were made over the flight path under standardized conditions. The resolution from all runs, regardless of film type, averaged between 28 and 32 lines per mm. This indicated that:

1. Direct correlation existed between the flight test performance and laboratory test performance.
2. The crushed dampers were limiting resolution during the flight tests undertaken during Phase III.
3. Environmental and weather factors at either 7,000 or 14,000 feet had not degraded camera performance.

Phase VI — Flight Trials

It was desirable to substantiate the laboratory findings by a further series of flight tests, during which the components of the camera and mount responsible for degradation were eliminated. This was accomplished as follows:

Shutter unit—The between-the-lens camera shutter was immobilized and left permanently open. Another shutter was placed below the lens and pulsed

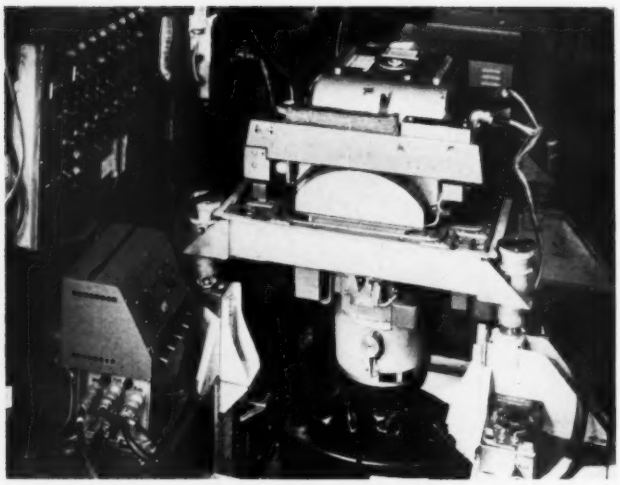


Fig. 6a. C-47 aircraft installation Type K17C F/L 24-inch camera with external shutter.

Fig. 6b. Intralens shutter adapted for use as an external shutter.

in the normal way. Light-tight bellows were placed between the shutter and the lens.

Weight Balance Shift Motors—These motors are required only to correct any unbalance caused by the passage of film from one side of the magazine to the other. It was decided therefore that the amplifiers which control the weight shifters should be removed before a photographic run and replaced afterwards to correct the imbalance created by the transfer of the small amount of film used during the run.

Magazine Motor and Platen—In the more common of the two current methods of IMC, the film is moved within the magazine at the required speed. This calls for magazine motor operation and sometimes the physical movement of the platen as well as of the film. This method was employed in the Type A-18 magazine used in this study. The second method involves swinging the camera to compensate for image motion. Here the film is stationary in the magazine at the time of exposure and therefore the magazine motor is operated only to advance the film after each exposure. For this reason, it was decided to modify a Type LS-6 mount to provide for the swinging mode of operation. All the known mechanical factors which degraded resolution within the camera system could be eliminated by means of these modifications. The ultimate performance of the system would then be influenced by the following factors:

1. Lens/film/aperture combination
2. Efficiency of the swinging mount
3. Accuracy of the IMC value applied to the mount
4. Efficiency of the vibration isolators

The efficiency of the vibration isolators was questionable and although the tests had shown that they did not depress resolution below 32 lines per mm they could be suspected of limiting performance at higher levels. Thus more efficient camera isolation was considered desirable.

The vibration characteristics at the camera position in the aircraft were determined and a set of spring and dash pot-type dampers were fabricated to suit these characteristics. In subsequent laboratory tests they proved superior to the isolators used previously, though not necessarily adequate for high-resolution photography. They were too large to install directly at the existing isolator positions on the mount, so a frame was made to which the dampers were secured. The mount was allowed to sit in this frame during photography.

It was not possible to fly the new camera configuration at this time because the swinging modification to the Type LS-6 mount had not been completed. It was decided, however, to experiment with an external shutter before the swinging mount became available. The Rapadine intralens shutter designed for use with a 36-inch focal length $f/4$ lens was the most suitable, since it could be placed on the camera window frame without obstructing the lens. The diameter of the shutter aperture was 7 inches and the highest shutter speed setting was $^1/_{50}$th second. The measured shutter speed was $^1/_{35}$th second. A light-tight black plastic bellows was secured to the shutter and the lens housing; care was taken that this arrangement did not at any time restrict camera stabilization. Figure 6 shows the external shutter installation.

It was decided to carry out all future flight tests with the experimental Kodak high-resolution film SO-1182, which is a panchromatic, Microfile-type film with an approximate exposure index of 10. It was processed in a B-5 processor with D-76 developer to a gamma of 1.3, later reduced to 1.2.

Phase VII — Flight Trials (External Shutter)

Three missions were flown with the external shutter installation. The average image resolution was a

disappointing 35 lines per mm, but target images on some negatives showed a resolution of 45 lines per mm, indicating a slight improvement over the standard installation previously flown during Phases III and V. Examination of the targets recorded on the negatives revealed that vibrations across the line of flight were primarily responsible for the losses.

Although the motor of the magazine restricted the performance to approximately 48 lines per mm, there was the additional unknown factor of the movement of the film platen which could be expected to lower the resolution below this value. Therefore, a new magazine of the same type, which had not been previously flight tested, was calibrated for use with the remainder of the test equipment and then flight tested. The smallest patterns on the airfield resolution target recorded within 6 degrees of the center of the format were resolved, indicating a high contrast resolution of at least 58 lines per mm. Marginal resolution at 10 to 12.5 degrees indicated a resolution of 33 to 41 lines per mm. It is probable that a pattern one size smaller, had there been one available, would also have been resolved, which would have given a resolution of 63 lines per mm.

External Shutter Aerial Photography

Relatively high resolution was obtained from the experimental installation, and the advantages of the external shutter were manifest. The quality of the recorded image had almost doubled and was three to four times the quality of the average Air Force aerial photograph. It should not be inferred from this that the shutter alone was responsible for the improvement. High quality optics, fine grain film, and attention to detail were other essential ingredients.

The Shutter

The shutter in the present installation is a fixture over the camera window. The camera, on the other hand, is stabilized. Aircraft pitch or roll therefore moves the axis of the lens off the center of the shutter, and under some conditions of flight causes vignetting and cut off. Of approximately 640 negatives exposed in this way, only 20 suffered from slight cut off. This low percentage can be attributed to the fact that the diameter of the shutter diaphragm was 3 inches larger than that of the lens (7 inches versus 4 inches). The distance between the lens and the shutter blades should be held to a minimum.

One of the problems in aerial photography is that of veiling glare and external reflections which may impair image quality, especially at high-resolution levels. The external shutter configuration tends to restrict all light from entering the lens other than that required to form the image, thereby reducing the effect of veiling glare and external reflection. This configuration should greatly improve the quality of night photography obtained by illumination from pyrotechnics.

Careful examination of the negatives by photographic interpreters has failed to reveal any signs of distortion that might interfere with intelligence extraction. The use of such a configuration for mapping is clearly undesirable, however, because increase in distortion is possible.

The Film and Filter

The Eastman Kodak Company has recently produced a series of experimental aerial films including SO-1182, that have steeper gradation than currently standard aerial materials. This is most desirable, especially in high altitude photography. In these tests, the photographs were taken from heights of 7,000 and 14,000 feet in clear weather. The first results obtained with the SO-1182 film suffered from excessive contrast, in spite of a reduction in gamma from 1.5 to 1.3. Thereafter, image contrast was reduced further by decreasing the gamma value to 1.2 and by removing the minus blue filter. This, in turn, almost doubled the effective speed of the film and allowed use of a more efficient lens aperture. (The use of filters with modern, high-contrast aerial films for high, medium, and low altitude photography might well be investigated by means of practical flight tests which should be flown under a variety of weather conditions.)

Exposure

It may be thought that a shutter speed of $^1/_{35}$th second was unrealistic and not compatible with modern trends in aerial photography, but such a slow shutter speed proved quite realistic so far as the camera itself is concerned. The system, however, must be efficiently steadied and free from internal vibrations.

The main reason for using a slow shutter speed, apart from the fact that it was the only speed available at the time, was that it reveals more readily the presence and character of vibrations. If some vibrations can be detected, analyzed, and eliminated for slow shutter speeds, there will have been removed possible limitations to securing higher resolution at faster shutter speeds at which vibration analysis becomes more difficult.

Resolution and External Shutter Camera Performance

High contrast resolution targets were used throughout the study. The main reasons for choosing this criterion of performance evaluation were:

1. Slight changes in performance are readily detected.
2. The contrast of the target images is such that smear caused by vibrations, incorrect IMC, etc., is easily analyzed.

Correlation between high-contrast resolution recorded under laboratory conditions and that obtained from aerial photography taken at 7,000 and 14,000 feet is good despite the slightly lower contrast of the target images recorded during flight trials. Whether correlation will remain satisfactory at higher resolu-

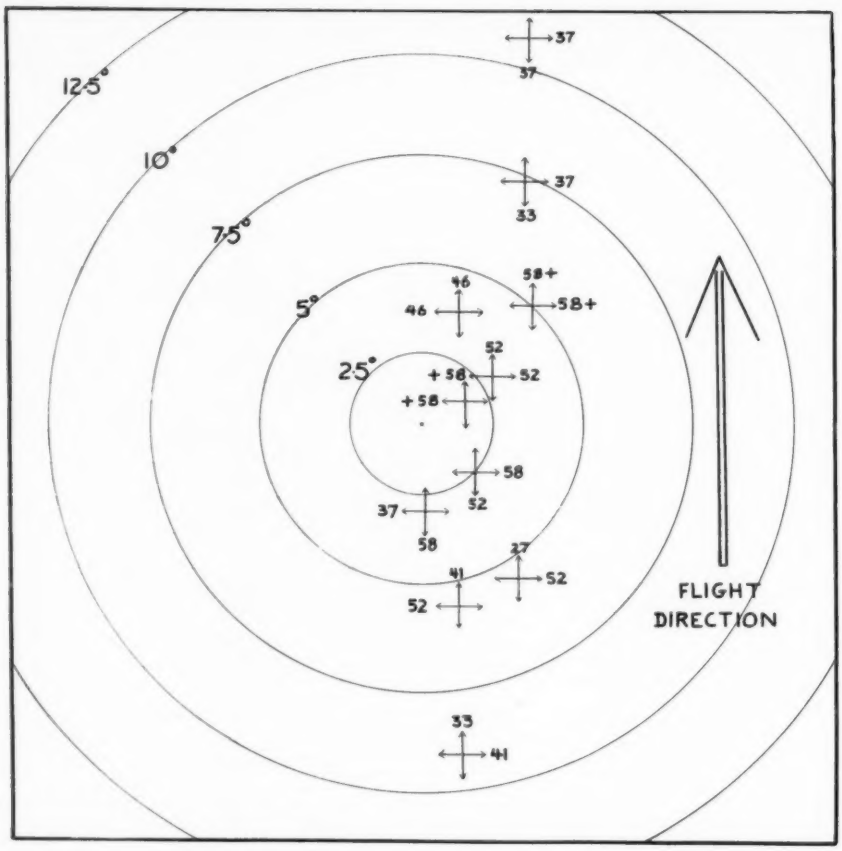


Fig. 7. Target composite (Run 5, 24 July 1957).

tion levels and for higher altitude photography remains to be determined.

Correlation of Flight and Laboratory Resolution

Transparent grids were produced which indicated the laboratory (static) resolution at each 2.5 degree zone across the 9- × 9-inch negative area. A separate grid was produced for each film type and lens aperture at which the film was tested. Correlation of static and flight resolution was obtained by placing the appropriate grid over an aerial negative and noting the resolution values of the target images and the corresponding zones of the grid. It was thus possible to determine the percentage loss of resolution at any part of the negative.

The final values were obtained by averaging the tangential and the radial readings obtained from all the negatives in any one run that contained images of the resolution targets.

Figure 7 shows the actual tangential (in line of flight) and radial (across line of flight) resolution values obtained from one series of negatives (SO-1182 film exposed at $f/11$ and $^1/_{35}$th second). The relative position of the various targets recorded on the different negatives have been transferred for convenience to a common grid that represents the format of the camera. The + sign beside some of the 58 lines-per-mm figures indicates that the smallest available target was fully resolved and that a still smaller target might have been recorded satisfactorily.

The static and flight resolution values have not yet been correlated for the SO-1182 film and lens aperture ($f/11$) at which the aerial photographs were made, though it is believed that the static, axial resolution is more than 100 lines per mm. If this is so, then vibrations are still limiting the performance of the system to approximately 58 lines per mm at the axis. This was to be expected, since the magazine motor vibrations had not been removed at that stage.

The Magazine

Laboratory tests undertaken in Phase IV indicated that the magazine then in use would limit resolution to 48 lines per mm, owing to vibrations induced by the motor. Flight trials made with the external shutter and with the same magazine during Phase III yielded a resolution limit of 35 lines per mm. The additional decrease in resolution could have been caused only by the film platen mechanism.

When a new magazine was selected and flight

tested with the external shutter, resolution increased to 58 lines per mm, or 10 lines per mm above that of another magazine of the same type. This indicates that the performance of a K 17C F/L 24-inch camera cannot be specified on the basis of the laboratory performance of only one unit. Probably at least five samples of any given component should be evaluated and the average considered an index of performance.

Image Movement Compensation

To achieve a high-contrast resolution value of 58 lines per mm at a shutter speed of $^1/_{35}$th second and under the specified conditions of flight, it is necessary to achieve an IMC accuracy of at least 3.25 per cent at the film. The accuracy must be increased to at least 1.95 per cent to obtain 100 lines per mm under the same operating conditions. This is a problem clearly outside the scope of this study, though unfortunately the damaging effects of inaccurate IMC cannot be ignored when they tend to obscure the ultimate performance of the camera.

The following factors were taken into consideration in an effort to increase the inherent accuracy of IMC in the system:

1. IMC speeds are directly influenced by the input a-c voltage to the magazine amplifier. Voltage was therefore monitored by the camera operator who maintained it at 120 volts during photography.
2. All IMC components, such as the camera control, magazine amplifier, and magazine, were calibrated before flight at 120 volts a-c to insure operation at optimum IMC accuracy at the small range of velocity/height (V/H) settings to be used in the air.

A type B-5 driftmeter was used to obtain the V/H value, but it was not as accurate as required, especially at the high resolution achieved during the later phases of testing. Therefore, the navigator took several V/H readings over the photographic flight path and their average value was set on the type C-4 control. Here, again, inaccuracies were bound to develop, because the 10 mph divisions on the ground speed scale of the control were only $^5/_{64}$th inch apart. Therefore the computed V/H value was bracketed by flying additional runs at adjacent values. This procedure, though expensive in flying time and film, proved worth while.

Flying for this type of photography when the slow shutter speeds are used must be perfect since any small changes in altitude or airspeed or the presence of yaw during the exposure period will significantly affect photographic image quality. The problem will become even more acute at higher resolution levels if the shutter speed is not increased and other means found for determining a more accurate V/H.

Projected Testing

In the next phase of the program, the swinging version of the Type LS-6 stabilized camera mount now being manufactured will be evaluated. This system will make it possible to transfer the IMC function from the magazine to the mount and thereby to eliminate the remaining source of internal vibration in the camera. All mechanical operations will then be at rest during exposure.

Whether the efficiency of the swinging mount will permit still higher resolution remains to be seen. Vibration isolation may again become a problem at a higher resolution level and steps have already been taken to incorporate a more efficient type of isolator into the mount. If the IMC error cannot be eliminated at the existing shutter speed of $^1/_{35}$th second at the expected higher resolution level, then the speed will be increased to $^1/_{70}$th or even $^1/_{100}$th second, with the adoption of another shutter which is presently being modified. This will have an adverse effect on the lens/film resolution performance because of the inefficient aperture which must be used ($f/6$ or $f/8$). It is hoped, however, that the reduced performance will not fall below the practical capability of the system.

The final phase of the study will involve the transfer of the equipment to an RB-57 aircraft. The characteristics of the aircraft vibrations at the camera position will be determined and some form of suitable isolation made. Flights will again be made over the Wright Field resolution targets at high altitude. The V/H factor will be calculated by coordination between the aircraft and ground radar and then passed to the aircraft in accuracies which will eliminate the IMC variable.

Conclusions

Air Force requirements apparently will be met in the near future with a photographic system that is essentially simple and free from both external and internal vibrations. The study indicates that far more importance should be attached to the selection and testing of vibration isolators. These apparently simple fixtures can ruin high-resolution photography if they are not matched to the weight of the system and the aircraft vibrations which they are to absorb.

It is not implied that the future high-resolution system should necessarily have an external shutter, nor that IMC should necessarily be controlled by swinging the camera. These modifications have been made to verify data collected during the course of the study. It is believed that other solutions may be equally effective. It is noteworthy, however, that tests already undertaken have shown that high contrast resolution values of about 60 lines per mm are attainable with current equipment.

Acknowledgment

The author wishes to express his thanks to Paul L. Stratton for his excellent work in connection with the interpretation of the large volume of negatives collected. Credit is also due to T/Sgt. F. W. Hoffman, USAF, who maintained and operated the camera equipment; and to the many other individuals of Aerial Reconnaissance Laboratory, WADC, who have contributed to this study.

PHOTOGRAPHIC SCIENCE AND ENGINEERING
Volume 1, Number 3, January 1958

• Technicalia Photographica

FRANK SMITH

• Cameras, Components, and Accessories

Combination Binoculars and Camera

Recent reports from Europe disclose some details of a high-grade 7 × 35 prism binocular which differs from similar instruments only in that it has a built-in camera. The binocular lenses are used for viewing and as a range-finder for camera focusing. The camera itself is equipped with a special 90mm focal-length lens that is interchangeable with lenses of 135mm or 50mm focal length.

The camera is precision built and is mounted between the binocular barrels. It contains a metal focal plane shutter with speeds from $^1/_{30}$ to $^1/_{800}$ second, a bulb setting, and "M" and "X" synchronization. Shutter and film winds are interlocked. The camera accepts double cassettes of unperforated 20-exposure 16mm film. The image format is 10 × 14 mm.

The Cam Binox is manufactured by the Optical Works J. D. Möller, Wedel, Holstein, Western Germany.

New 35mm Camera

A new low-cost camera for color photography has been announced by the Argus Camera Division, Sylvania Electric Products, Inc. It is called the Argus C-20 and is equipped with a lens-coupled range-finder and lever wind for rapid film advance. With the aid of "Color-matic" settings, the correct exposure can be selected almost automatically for average subjects in bright sunlight.

The C-20 camera permits focusing from $2^1/_2$ feet to infinity and features also a coated and color-corrected $f/3.5$ Cintar lens with click-stop aperture settings to $f/22$ and click-stop shutter settings from $^1/_{25}$th to $^1/_{200}$th second.

The molded body weighs 16 ounces and is finished in two-tone brown with leather grain and satin metal trim. A complete kit is available that includes everything needed to take and view color slides—the C-20 camera, Argus previewer, plug-in flash unit, photoflash batteries, color film, and Sylvania Press 25B flash bulbs.

2¼- × 2¼-inch Hand-Held Aerial Camera

A new $2^1/_4 \times 2^1/_4$-inch hand-held spring-driven aerial camera is being imported from Japan and made available by the Konica Camera Co., 76 West Chelten Ave., Philadelphia 44, Pa. The principal features of the camera are a Hexanon $f/3.5$ 135mm or Hexanon $f/3.5$ 85mm lens, aperture settings from $f/3.5$ to $f/22$, and shutter speeds from $^1/_{50}$ to $^1/_{400}$ second.

The camera accepts standard No. 120 size roll film and yields ten $2^1/_4 \times 2^1/_4$-inch photographs. It measures $9^3/_4 \times 6^3/_4 \times 6$ inches and weighs 6 pounds.

The camera is equipped with an automatic film counter, a sports-type viewfinder, contour-molded hand grips, and a large handle underneath the camera for winding the spring. Three filters, a lens cap, neck strap, and leather case are standard equipment.

Lightweight Panoramic Camera for Aerial Reconnaissance

A precision-built, high-resolution camera, Model 501, which yields horizon-to-horizon photographs has been developed by the Perkin-Elmer Corp., Norwalk, Conn. The camera employs a scanning device to produce successive 180-degree panoramic photographs. It is an automatic sequencing camera with sufficient film capacity to provide horizon-to-horizon coverage for a complete aerial reconnaissance mission.

The Model 501 camera weighs less than 53 pounds fully loaded and is only 7 inches deep. It contains built-in image motion compensation, intervalometers, automatic aperture controls and other devices necessary for high quality images. The camera is operated on 28-volt d-c and accepts 1,000 feet of 70mm standard base film, with MS 33525 perforation, on special spools.

In the two consecutive exposures shown here, the bright circle below the center of each photograph is a clock showing the time of exposure. The gridded circle with black dot, at top, indicates that the camera was stabilized and mounted level. The photographs were taken from a jet fighter flying at 7,000 feet.

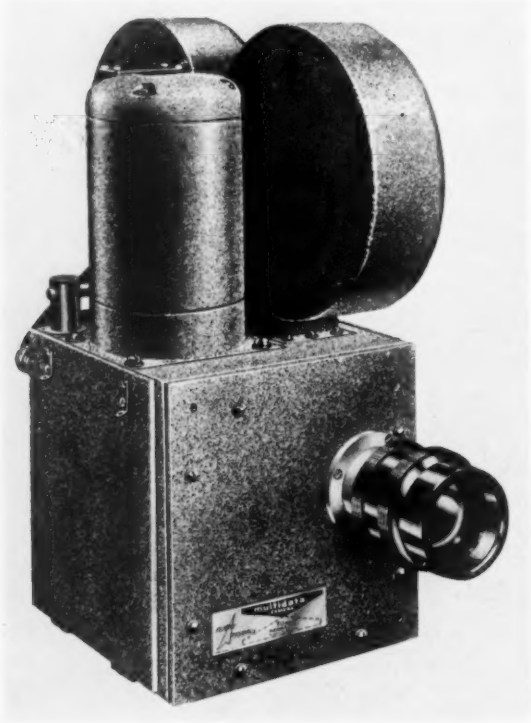
A New Shoulder-Mounted Tracking Camera

A. M. Erickson and C. G. Grover, *JSMPTE*, Vol. 66, pp. 484–486 (Aug. 1957).

A new shoulder-mounted instrumentation camera has been designed and constructed by the Naval Ordnance Laboratory for tracking high-speed, air-laid ordnance. The requirements arising from the problems of tracking falling missiles, and the features needed by field evaluation groups, are discussed and the usefulness of the camera is compared with that of earlier models.

70mm Missile-Tracking Camera

The Multidata Model V, a new 70mm camera for missile tracking, has been announced by Flight Research, Inc., Richmond, Va., which also makes the Multidata Model IV-C 35mm and Model III 16mm cameras. The Model V camera offers the advantages of larger image format and greater magnification than the earlier, smaller-size models, and facilitates tracking of high-speed missiles. Moreover, the greater magnification permits more detailed study of fin flutter, attitude, exhaust nozzle characteristics and exhaust patterns, and of other component features. A new film drive combined with registration pins insures precise frame-to-frame alignment, while reduced vibration permits high image resolution even at speeds of 60 frames per second, and at shutter openings of 120 degrees.



Two neon lights produce code marks on both edges of the film for time base correlation and four lighted fiducial markers indicate the aperture centerlines to within 0.001 inch. The shutter is adjustable from 0 to 120 degrees and at any setting a pulse is generated at the midpoint of the exposure period. A removable lens board is incorporated also.

Earth Satellite Optics by Zoomar, Inc.

A set of two-element high-speed lenses with a 3-inch plastic Fresnel front element and a small glass rear element has been developed by Zoomar, Inc., Glen Cove, N.Y., for use on earth satellites.

The lenses will be mounted opposite each other and will face the earth's surface alternately as the satellite rotates. The lenses, including the housing, have a speed of $f/0.7$ and weigh $2\frac{1}{2}$ ounces each. Infrared radiation reflected from clouds will be focused by the lenses into a very small detector unit. Solar batteries inside each unit will activate each unit as it faces the earth's surface, and will turn off the equipment when the satellite is on the dark side of the earth. The weather information collected by the devices will be telemetered back to earth.

The 41st Physical Society Exhibition 1957

R. E. Stapleton, *J. Phot. Sci.*, Vol, 5, pp. 96–97 (July-Aug. 1957).

A brief report about the photographic equipment exhibited at the 41st Physical Society Exhibition in England. Among the items described is a 12-camera unit for recording 12 successive frames at adjustable intervals from a fraction of a microsecond to a millisecond, by means of a Kerr cell shutter system. The camera was designed by the Armament Research and

Development Establishment for photographing self-luminous events associated with explosions.

Other items shown were Dr. J. S. Courtney-Pratt's high-speed camera; also a high-speed camera with five lenses that are opened in turn by means of a special shutter arrangement synchronized with a bank of 100-joule short-duration flash tubes to give exposure rates up to 1000 pulses per second. The latter camera was developed by the Admiralty Research Establishment.

• Illumination

Air Force Night Aerial Photography System

An experimental, continuous high-intensity illumination system for aerial night photography has been announced by the U.S. Air Research and Development Command.

Present night photography systems are dependent on flash bombs or cartridges that produce a brilliant flash lasting only a fraction of a second; moreover, their light is dissipated in all directions. The new system, developed by ARDC's Wright Air Development Center, Dayton, Ohio, utilizes a commercial high-intensity mercury arc lamp to provide a narrow, directed beam of continuous light. Although the active element of the lamp is no larger than a cigarette, it yields sufficient light for aerial photography. Excellent photographs have been obtained with this system at various altitudes and speeds.

The new light source eliminates the heavy and bulky equipment needed with pyrotechnic sources, is much less expensive, and is safe, since explosives are not used. Furthermore, the reconnaissance aircraft equipped with a mercury arc lamp is limited only by the range of the aircraft and the film capacity instead of the number of flash bombs that can be carried.

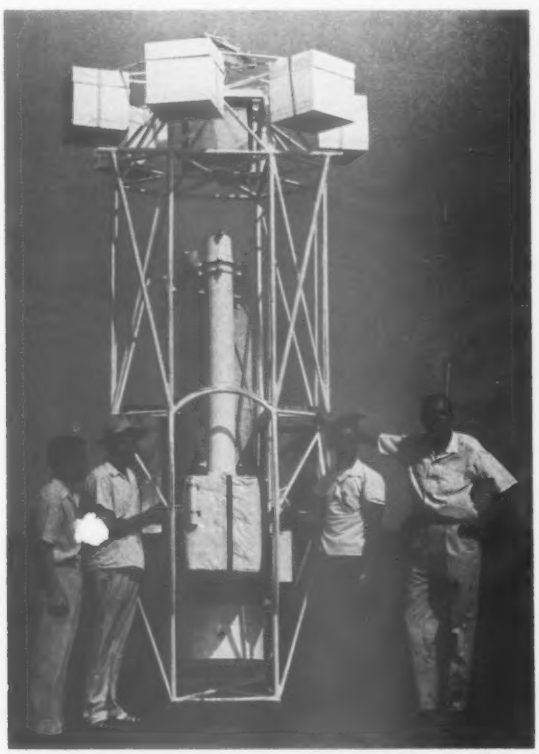
• Instrumentation

Photographic Instrumentation of Navy Project Stratoscope

A recent news release from the Office of Naval Research, Washington 25, D.C., contains some details about the photographic instrumentation of project Stratoscope, a balloon-borne telescope system designed for high-altitude studies of the sun, moon, planets, stars, and spiral nebulae. The initial flights are planned to secure high-quality photographs of the sun.

The Stratoscope system consists of a giant unmanned polyethylene balloon which carries to heights of at least 80,000 feet a powerful, specially-designed, 12-inch astronomical telescope coupled to a 35mm motion-picture camera and a light-sensitive pointing mechanism. When the balloon has ascended to sufficient height and the telescope is oriented to face the sun, the camera takes approximately 8,000 photographs at the rate of one per second.

On a recent successful ascent over New Brighton, Minn., the balloon carrying the telescope ascended



Official United States Navy Photograph

to a height of 81,000 feet and some 8,000 pictures were taken of a segment of the sun. The pictures, which are the best close-ups of the sun ever taken, disclosed some hitherto unknown details.

The primary contractor for the solar instrumentation phase of this project is the Princeton University Observatory. Others participating in the work are the University of Colorado and Perkin-Elmer Corp.

• New Materials

New Kodak Films for Aerial Photography

Kodak Plus X Aerecon Film and Kodak Tri X Aerecon Film, two new and improved aerial photographic materials, have been announced by the Eastman Kodak Co., Government Sales Division, Rochester 4, N.Y.

Plus X Aerecon Film is designed for high-altitude work. It is about a third of a stop slower than Kodak Super XX Film and its spectral sensitivity extends to 710 μ. Its acutance is said to be very much higher than that of Super XX film and to remain high at great image densities. Plus X has higher resolving power than Super XX in the ratio of 9:8 for a test contrast object of 1000:1 and in the ratio of 3:2 for a test object contrast of 2:1.

The spectral sensitivity of the new Tri X Aerecon Film also extends to 710 μ and it has twice the speed of Super XX. Both films can be processed in solutions at up to 90 F.

• Optics

The Spectral Reflectivity of Back Surface and Surface Aluminized Mirrors

G. G. Twidle, *Brit. J. Appl. Phys.*, Vol. 8, pp. 337–339 (Aug. 1957).

Data are presented on spectral reflectivity of back- and front-aluminized quartz mirrors in the wavelength range 0.25–1.35 microns. Illustrated. 7 references.

Hydrothermal Sapphires for Optics

It is reported (*Chem. & Eng. News*, Sept. 23, 1957) that at the Bell Telephone Laboratories synthetic sapphires have grown as large as $^3/_4 \times {}^3/_4 \times {}^1/_4$ inches. Unlike flame fusions and melt techniques, the new process is said to give crystals that seem essentially free of strain; therefore, these crystals may prove useful for lenses, prisms, and other optical items.

Relative Stress – Optical Coefficients of Some National Bureau of Standards Optical Glasses

M. Waxler and Albert Napolitano, *Jour. Research Nat. Bur. Standards*, Vol. 59, pp. 121–125 (Aug. 1957).

A brief review covering the relative stress-optical coefficients of 27 optical glasses which have been determined by the National Bureau of Standards. Illustrated. 15 references.

• Photomechanical Processes

The McCorquodale-Gresham Process for Colour Photogravure

D. C. Gresham, *J. Phot. Sci.*, Vol. 5, pp. 89–93 (July–Aug. 1957).

In the conventional photogravure process, printing is from etched cylinders in which the printing areas are depressed below the surface. The image is divided into small cells which vary in depth, in accordance with the tone value to be printed, but have substantially constant area throughout the tone range. There are definite advantages in using a system in which both the depth and the area of the printing cells are varied and, as an example of this, the Dultgen process is described. A further advance has been made in the McCorquodale-Gresham process, in which a screen positive of special characteristics is made from a finished continuous tone positive by reversal processing. Both the continuous tone and the screen positive are then used to produce a printing cylinder. 2 references. Illustrated.

• Projection

New Kodak 16mm Projector, Model 25B

The Kodak 16mm projector for auditorium and theater use is now available in a model which is said to offer 20 per cent more illumination than the

former model and which may be adapted for magnetic as well as optical sound. Standard equipment on Model 25B is the newly-developed Kodak Optical-Magnetic Pre-Amplifier, which will accommodate the signal output of a magnetic sound head as well as that of the standard optical system. Reproduction of magnetic sound with the projector may be accomplished by field installation of another new accessory device, the Eastman Magnetic Sound Playback Kit.

The Model 25B Projector may be had with either tungsten or arc light source. The tungsten lamp unit yields a minimum illumination of 550 lumens. The arc model produces a minimum illumination of 300 lumens without heat-absorbing glass for color film and 2400 lumens with heat-absorbing glass for black-and-white film. The power output of the main Altec-Lansing amplifier has been increased from 15 to 30 watts, with the result that harmonic distortion has been reduced substantially. Retained are other features of previous Kodak 16mm Projectors, such as: Kodak Projection Ektar Lens; 46-amp Strong Electric Corp. arc lamp; microphone or phonograph input; and Altec-Lansing "Voice of the Theater" speaker.

• Sensitometry

Xenon Electronic Flash Sensitometer

Charles W. Wyckoff and Harold E. Edgerton, *JSMPTE*, Vol. 66, pp. 474–479 (Aug. 1957).

An intensity-scale xenon flashlamp sensitometer is described that is useful for black-and-white or color process control work. Three exposure settings, $^1/_{100}$, $^1/_{1000}$, and $^1/_{10,000}$th second, cover the range of shutter speeds used in normal and high-speed photography and permit evaluation of films under all of these operating conditions. The color quality of the light emitted by the flash tube approximates daylight and the light output is very uniform.

Photographic Sequence Exposure Experiment

J. H. Enns and E. Katz, *J. Opt. Soc. Amer.*, Vol. 47, pp. 758–764 (Aug. 1957).

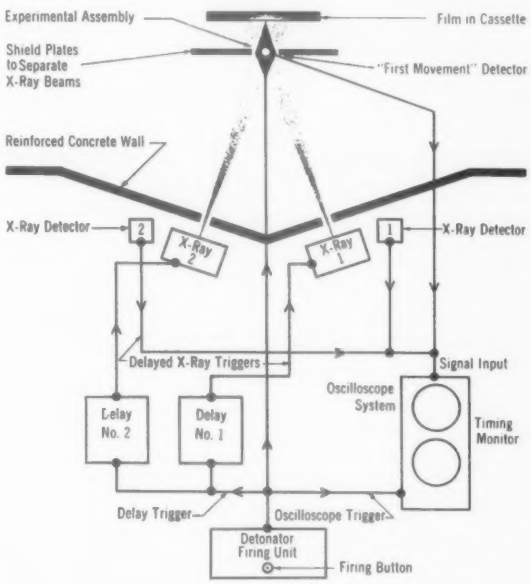
An instrument intended for automatic sequential exposures on 4- × 10-inch photographic plates is described. Twelve shutter slides are independently timed so that on one plate up to 384 rectangles measuring 4 × 5 inches each can be uniformly exposed to high- and low-intensity radiation. The present design is for an intensity ratio of 100:1, where both intensities are below optimum. With minor modifications the instrument can be converted to operate at other intensity ratios. The densitometer readings are checked from calibration strip data placed adjacent to the sequence exposures. The corrected data, following conversion to Seidel Values, are plotted as families of characteristic curves, with the sequence exposure ratio as the constant parameter. Isodense loop data are read from the curves at the intersections with a line drawn parallel to the exposure axis. Illustrated. 6 references.

• Techniques and Applications

Shadow Pictures for Explosives Research

Anon., *Research for Industry*, Vol. 9, No. 5, pp. 4–5 (Sept. 1957).

A brief account of an ingenious double-flash x-ray technique used to obtain radiographs of detonating explosive charges which are often obscured by gas, smoke, and flame. Two x-ray tubes are employed that fire in sequence at pre-set times to send high-intensity beams through the elements of an exploding test



charge and create shadowgraphs on a film mounted behind the test assembly. The technique was developed by the Poulter Laboratories of Stanford Research Institute, Menlo Park, Calif., under the sponsorship of the U.S. Army Ordnance Department. Illustrated.

Rocket and Satellite Cinematography

A. R. Michaelis, *Brit. J. Phot.*, Vol. 104, pp. 374–383 (June 28, 1957).

The Askania ciné-theodolite, which was first described in 1929, records azimuth, elevation and time data of airplane and missile flights. Since the introduction of ciné-theodolite, cinematography has played an essential part in the development work of rockets. This illustrated review of American articles on the subject includes descriptions not only of launching operations and tracking, but also of recording of instrument panels and the analysis of rocket-motor flames using a spectrograph-camera combination. [*Ansco Abstracts*, Aug. 1957, p. 319, Abstract No. 876]

Microfilm Reader-Printer Enlargements

A machine that prints enlargements from microfilm files automatically in less than 10 seconds has been announced by the Duplicating Products Division of Minnesota Mining and Manufacturing Co., St. Paul, Minn.

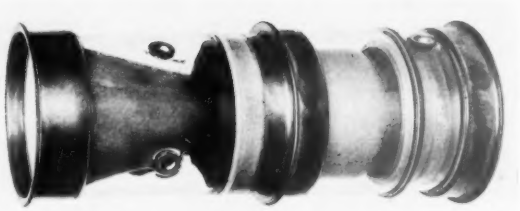
Called the 3M Brand Microfilm Reader-Printer, the machine is both a reader and a printer in a single unit, and is completely automatic, eliminating hand processing of prints. It projects microfilm on a viewing screen in the usual manner for reading, and when a button is pressed, produces a ready-to-use print in less than 10 seconds. This is claimed to be six to eighteen times faster than other methods. The machine prints by an automatic electro-chemical process on a special white paper, $8^1/_2 \times 11$ inches or $8 \times 10^1/_2$ inches. The speed and simplicity of automatic printing solve a major problem in using microfilm for "active files," it is claimed.

The reader-printer operates on 110 volts a-c. It can be placed anywhere in an office and requires no running water, darkroom, or other special facilities. The only material required for operation is a roll of 3M microfilm print paper and a cup of 3M developer chemical. The reader-printer is equipped with a lens for either 16mm or 35mm film, or both. Size is 25 $\times$ 17 $\times$ 19 inches and weight is 85 pounds.

Experimental RCA Tube for High-Speed Photography

Multiple-frame photography of events occurring at high speed with exposures as short as one-hundred-millionth second is possible through the use of a new image converter tube now under development by the RCA Electron Tube Division, according to G. W. Duckworth, Marketing Manager, Industrial Tube Products, Harrison, N.J.

The new tube has electrostatic focus, a grid which functions as a shutter, and a deflection system which



can produce as many as five separate screen images at one time. The event or action is focused on the photocathode of the tube by means of a fast objective lens. The light striking the photocathode produces electrons which are attracted at high velocity toward the fluorescent screen at the opposite end of the converter. In their passage, the electrons first encounter a fine metal mesh called a gating grid. This grid may be charged either to repel the electrons emerging from the cathode or to permit their travel toward the screen; it is also used to focus the electrons on the screen.

After passing the gating grid, the electron beam is directed through a small aperture to a set of deflecting electrodes. Proper design of these electrodes makes it possible for the beam to be deflected over a wide angle without distortion or loss of resolution. The electron beam energy is converted by the phosphor screen into actinic radiation. The screen is prepared with a very fine-grain phosphor and is backed with aluminum to increase light output. Under normal operating conditions, the tube can provide an increase in radiant energy emitted from the screen of as much as 24 times the radiant energy incident on the photocathode.

Development of the tube was sponsored partly by the University of California under AEC contract but many of its features embody the results of earlier research and development sponsored by the U.S. Army Engineer Research and Development Laboratories, Fort Belvoir, Va.

The Loading of Nuclear Emulsions with Water

C. J. Batty, *Nuclear Instruments*, Vol. 1, pp. 138–142 (May 1957).

The rate of absorption of water by G-5 emulsions has been studied at temperatures between 6 C and 18 C and the relation between swelling and water content determined.

The volume of the swollen emulsion is generally less than the sum of the volumes of water and dry emulsion, and this can affect cross-section measurements. The grain density of 540-mev proton tracks falls by about a third when 3 g of water are absorbed in 1 ml of dry emulsion. An area scan for p-p elastic collisions gives, as expected, a reduced ratio of background events in the loaded emulsion. Illustrated. 8 references.

The Time-Dependence of the Recording Properties of G-5 Nuclear Emulsion

W. C. Barron and A. W. Wolfendale, *Brit. J. Appl. Phys.*, Vol. 8, pp. 297–300 (July 1957).

The fading of fast proton and μ-meson tracks in G-5 nuclear emulsion has been studied as a function of time and conditions of storage. The storage time for a 50 per cent reduction in the blob density of the tracks is estimated to be 1040 ± 200 days for storage at 5 C and 520 ± 50 days at 25 C. No difference in fading has been found between the emulsions stored in air and those stored in commercial argon. The mechanism responsible for the fading appears to be the thermal ejection of electrons from the latent image. The sensitivity of the emulsion after storage has also been studied. A reduction of less than 5 per cent has been found in blob density of the tracks of fast particles after a storage time of 450 days. Illustrated. 8 references.

Microcite — An Aid to More Effective Referencing

Anon., *NBS Tech. News Bul.*, Vol. 41, pp. 141–142 (Sept. 1957).

A brief report on Microcite, a method for making indexed information directly accessible and reproducible, which is being developed to increase the effectiveness of literature searching at the National Bureau of Standards. Proposed for use in the Bureau's instrumentation reference service, the Microcite feature consists of photographically storing greatly reduced copies of citations and abstracts (called microabstracts) so they can be readily located and read. Illustrated. 3 references.

Exploding Wire as a Light Source in Flash Photolysis

Gisela K. Oster and R. A. Marcus, *J. Chem. Phys.*, Vol. 27, pp. 189 (July 1957).

A review of experiments that have shown that an exploding wire is a light source of considerable brilliance and excellent reproducibility which should be useful in flash photochemistry. Since the wire is a small source, the light beam could be rendered very parallel by reflectors or lenses with the wire at the focal point. The spectral output of this source can be changed at will by choosing the appropriate metals (e.g., it was found that copper wire emitted very intense green light). Illustrated. 11 references.

The Photography of Electron-Optical Images

J. Smits, *The Engineers' Digest*, Vol. 18, pp. 248–251 (June 1957).

The procedure for photographing images obtained with an electron microscope and the subsequent processing of the photographic material are described. Particular attention is given to the points differing from normal photographic processes. Illustrated.

• Miscellaneous

Photo-Electronic Aids to Photography

J. D. McGee. *Brit. Kinemat.*, Vol. 30, pp. 165–176 (June 1957).

Use of the external photoelectric effect in Lallemand's telescopic camera of 1952, in Hiltner's photoelectronic camera, and in electron-image multipliers is discussed. This effect is more efficient than the photographic effect involving silver halides and shows no reciprocity failure even at the lowest light levels. Maintenance of the correct distribution of the electrons in the image of electron-image multipliers is still a problem. [*Ansco Abstracts*, Aug. 1957, p. 329, Abstract No. 904].

Electroluminescence and Its Applications

J. N. Bowtell, *J. Inst. Elec. Engrs.*, Vol. 3 (New Series), pp. 454–459 (Aug. 1957).

Phosphorescence has puzzled man from early times. The ghostly, wavering light of fireflies, glow-worms, and luminous fishes has aroused superstition, fear and curiosity. With increasing rationalism came the concept of "cold light," but not until the elucidation of atomic structure was any explanation even a possibility.

The author, who is with the Research Laboratories of the General Electric Co. at Wembley, describes the stimulation of luminescence by alternating electric fields, and the applications and limitations of the phenomenon. "Cold light" remains outside our grasp, but the search continues unabated. Illustrated. 14 references.

The Nature and Formation of the Photographic Latent Image

J. W. Mitchell and N. F. Mott, *Phil. Mag.*, Vol. 2 (Eighth Series), No. 21, pp. 1149–1170 (Sept. 1957).

Reviewed here are a theory of the nature and mode of formation of the photographic latent image and of the experimental evidence on which the theory is based. The authors use earlier hypotheses put forward by Eggert and by Gurney and Mott, according to which the primary action of the light is to free photoelectrons and positive holes, and the formation of silver specks involves the movement of silver ions. The stable latent image is seen as a positively charged silver speck on the surface of a halide grain, or, in the case of internal image, at a dislocation. The minimum stable image is a positively charged group of four silver atoms (Ag_4^+), the formation of which requires three electrons. The sub-image is a neutral pair of silver atoms and requires two electrons for its formation. A main role of silver sulfide is to provide traps for positive holes. After such trapping the sulfide molecule dissociates into AgS and an interstitial cation.

Reciprocity failure, development, and the role of iodide and of other phenomena are discussed in terms of this model. Illustrated. 57 references.

• Notes from the Editor

• Six issues of PS&E, that is, two issues of Volume 1 and four issues of Volume 2, will come to you during 1958. In this way, the unavoidably late start of publication of PS&E in 1957 will be overcome, and succeeding volumes will be issued on a calendar year basis.

• A change in the editorial staff deserves mention. Edward K. Kaprelian, who contributed the material for the Patent Postscripts feature, unfortunately has had to relinquish this assignment owing to new and more demanding work. His place will be taken by Dr. Robert H. Zappert, a chemist by profession and at present a member of the Patent Department staff of one of the photographic manufacturers. Bob's first contribution will appear in the next issue.

• Finally, a few words about the make-up of this journal. A good deal of planning preceded the selection of the format, the typography, the paper and all the other important details. Comments received to date indicate that the final choice has met with approval. A few modifications were made in the second issue and a change in the emblem is scheduled for the first issue of Volume 2. Other modifications could be introduced at that time. Your comments and recommendations are invited.

• Owing to an unfortunate mistake, the Abrams Instrument Corporation, a Sustaining Member of the Society, has been listed as the Abrams Aerial Survey Corporation in past issues of this journal. This error has now been corrected. — *Peter Krause*

1958 Annual Conference

6 to 10 October 1958

Manger Hotel • Rochester, N. Y.

The next Annual Conference of the Society has been scheduled for October 6 through 10, 1958, at the Manger Hotel (formerly the Seneca), in Rochester, N.Y. Planning for the Conference is well under way, with Ira R. Kohlman as Conference Co-ordinator. All inquiries about Conference matters should be sent to Mr. Kohlman, c/o Technicolor New York Corp., 533 West 57th Street, New York 19, N.Y., or to the appropriate chairman who is responsible for any one of the various phases of the program.

An extensive papers program, including a special group of papers pertaining to the IGY, is being prepared under the guidance of Jerome S. Goldhammer, CBS Research Laboratories, 485 Madison Avenue, New York 22, N.Y. There will again be exhibits of special photographic equipment, under the chairmanship of Richard van Steenburgh, Fairchild Camera and Instrument Corp., Robins Lane, Syosset, L.I., N.Y.

The Society of Photographic Scientists and Engineers

Box 1609 • Main Post Office • Washington, D.C.

OFFICERS

President	GEORGE T. EATON, Bldg. 59, Kodak Park, Rochester 4, New York
Executive Vice President	STEVEN LEVINOS, Ansco, Binghamton, New York
Engineering Vice President	JOHN A. MAURER, 116–118 West 29th Street, New York 1, New York
Editorial Vice President	PETER KRAUSE, 29–11 Bell Boulevard, Bayside, New York
Financial Vice President	HERBERT MEYER, 325 Sequoia Drive, Pasadena 2, California
Secretary-Treasurer	NORTON GOODWIN, 826 Connecticut Avenue NW, Washington 6, D.C.
Managing Secretary	EDWARD S. COBB, Box 1609, Main Post Office, Washington, D.C.

CHAPTERS *and* CHAPTER OFFICERS

Binghamton, New York	*President*	KEITH FAMULENER, 605 Main Street, Owego (Tioga County), New York
	Secretary	L. A. MICCO, 125 Leroy Street, Binghamton, New York
Boston, Massachusetts	*President*	LOUIS ROSENBLUM, Photon, Inc., 58 Charles Street, Cambridge 41, Mass.
	Secretary	E. FRANCIS MACNEILL, 253 Greendale Avenue, Needham 94, Mass.
Cleveland, Ohio	*President*	W. H. BOWERMAN, Box 154, Solon, Ohio
	Secretary	CLINTON K. HAMLINK, 2230 South Overlook Road, Cleveland 6, Ohio
Ithaca, New York	*President*	ARTHUR C. STALLMAN, 218 Waite Avenue, Ithaca, New York
	Secretary	DAVID O. FLETCHER, 1314 East State Street, Ithaca, New York
Monmouth, New Jersey	*President*	THEODORE E. CATELLI, 37 Brook Avenue, Little Silver, New Jersey
	Secretary	JOSEPH MANGIARACINA, 30 Brook Avenue, Little Silver, New Jersey
New York, New York	*President*	HENRY M. LESTER, 270 West End Avenue, New York 23, New York
	Secretary	RALPH R. BAUM, 319 East 44th Street, New York 17, New York
Rochester, New York	*President*	WILLIAM S. SHOEMAKER, Rochester Institute of Technology, 65 South Plymouth Avenue, Rochester, New York
	Secretary	ROBERT H. MAHER, Eastman Kodak Company, 343 State Street, Rochester 4, New York
Southern California	*President*	ROBERT O. MEASE, 1025 Via Zumaya, Palos Verdes, California
	Secretary	BERNARD A. AUGUSTINE, 235 Annandale Road, Pasadena 1, California
Southern Lake Michigan	*President*	N. W. RODELIUS, 2749 Reese Avenue, Evanston, Illinois
	Secretary	ROBERT J. MASOR, 1438 West 123rd Street, Chicago 43, Illinois
Washington, D.C.	*President*	HOWLAND PIKE, RFD 2, Silver Spring, Maryland
	Secretary	DWIN R. CRAIG, 815 Fisher Street, Falls Church, Virginia
Mid-Gulf Area	*Organizing Committee*	ROBERT E. LEWIS, CML, University of Chicago, Eglin Air Base, Florida

Sustaining Members / Society of Photographic Scientists and Engineers

Abrams Instrument Corporation

Ansco

Argus Camera

Charles Austin, Incorporated

Bar-Ray Products, Incorporated

Bausch & Lomb Optical Company

Bell & Howell Company

Charles Beseler Company

Cameraflex, Incorporated

Chemco Photoproducts Company, Incorporated

Chicago Aerial Industries, Incorporated

De Jur Amsco Corporation

E. I. du Pont de Nemours & Company

Eastman Kodak Company

Ednalite Optical Company, Incorporated

Elgeet Optical Company, Incorporated

Enteco Industries, Incorporated

Fairchild Camera & Instrument Corporation

Farrand Optical Company, Incorporated

Federal Manufacturing & Engineering Corporation

Oscar Fisher Company, Incorporated

The F-R Corporation

General Electric Company

Gordon Enterprises

Graflex, Incorporated

Grant Photo Products

W. & L. E. Gurley Company

The Haloid Company

Hardale Associates

Harris-Seybold Company

Horizons, Incorporated

Hycon Manufacturing Company

Houston-Fearless Corporation

Charles A. Hulcher Company

Philip A. Hunt Company

Kalart, Incorporated

Kollmorgen Optical Corporation

J. A. Maurer, Incorporated

The Morse Instrument Company

Nems-Clarke, Incorporated

Pako Corporation

Photogrammetry, Incorporated

Polaroid Corporation

Remington Rand, Incorporated

Simmon Brothers, Incorporated

Sun-Ray Photo Products, Incorporated

Technicolor New York Corporation

Wollensak Optical Company

Zoomar, Incorporated